

A COMBINED COURSE
IN
CHEMISTRY

VOLUME I

FOR PRE-ENGINEERING, PRE-MEDICAL
AND
FIRST YEAR OF THE 3-YEAR DEGREE COURSE

Written exclusively for the University
of Jammu and Kashmir

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PREFACE TO THE FIFTH EDITION

This book has now been in wide circulation for the last several years and has been serving the students of various universities in India including the University of Jammu and Kashmir. A suggestion was made to us recently by a number of chemistry teachers in various colleges in the state of Jammu and Kashmir to revise the book so as to cover *exclusively* the latest syllabus of their University. This has been done in the present edition.

The treatment has been brought up-to-date to suit the present requirements. The chapters on periodic classification of elements, atomic structure, valency, catalysis, oxidation-reduction and metallurgies have been dealt with in very lucid style and simple language keeping in view the difficulties commonly experienced by students at this age group in our country. In organic chemistry portion, the latest mechanisms of reactions have been added to serve as a background information for the teacher and a thought-provoking material to more curious and critical minded student who is looking forward to join higher classes. The chapter 'Typical reactions of various functional groups' given at the end, highlights the characteristic properties of organic compounds belonging to different categories and is likely to be useful to students for quick revision.

The authors earnestly hope that the present revised and improved edition will be warmly received and will prove beneficial to the students of the university of Jammu and Kashmir too.

Authors

March, 1968



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PREFACE TO THE FIRST EDITION

The recent change-over to the 3-year degree course in a number of Indian universities has necessitated revision and overhauling of the syllabi everywhere. The authors, therefore, need no apology to present the new chemistry syllabus in the form of a combined course in 3 volumes, one for each year. The 3 volumes, combined together, fulfil completely the requirements of the degree course of the Indian universities in all the three major branches of chemistry.

The present book, Volume I, of the series, is meant for the first year degree course as well as for the pre-engineering and pre-medical examinations. A concerted effort has been made to simplify the subject, as far as possible, keeping in view the standards attained by an average student who has just passed the pre-university or higher secondary examination.

The aim of the new orientation of the B.Sc. course, in particular, is to raise the standards of university education in science subjects. In order to realise this objective, the foremost thing that is needed is to provide suitable text books at a reasonable price. Further, as the modern trend is to encourage critical thinking and to bring out as well as to develop the latent creative faculty in younger people, a modern text book should contain precise and up-to-date information presented lucidly in a simple and clear language with a proper and orderly sequence. Every effort has been made to keep these requirements in view.

The authors earnestly hope that no material in this book will be such as cannot be understood by even an average student provided he makes an honest effort.

Suggestions for the improvement of the book will be thankfully received.

July 5, 1962.

Authors

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PART I
PHYSICAL
AND
INORGANIC

CHAPTER I

INTRODUCTION

Divison of Chemistry. During the last one century the knowledge of chemistry has grown so vast and the field has become so wide and complex that it is necessary to divide it into different branches for proper organisation and understanding of the subject. This division, however, is artificial and arbitrary because there is a considerable overlapping and the same fundamental principles are involved in all branches, which, in fact, "are like branches of a tree that join in one trunk."

The three major branches of chemistry are Organic, Inorganic and physical. **Organic chemistry** is confined to the chemistry of carbon compounds. **Inorganic chemistry** relates to the study of metallic and non-metallic elements and their compounds. **Physical chemistry** concerns itself with the study of physical properties and constitution of matter, the laws of chemical reactions and the theories governing these reactions.

The other branches of chemistry are : *nuclear chemistry* which deals with nuclear reactions, artificial transmutations of elements and radioactive isotopes ; *biochemistry* which describes reactions of living processes in health and disease : *analytical chemistry* which specialises in the various methods of analysis applicable to different types of compounds ; *industrial chemistry* or *technical chemistry* which applies principles of chemistry to the large scale manufacture of different elements and compounds ; and *agricultural chemistry* which is devoted to the study of soil, water, fertilizers and compounds recovered from plants. Some other branches such as *high-polymer chemistry*, *pharmaceutical chemistry*, *theoretical chemistry*, etc., are fast developing. Perhaps no other science to-day is so broad in its scope as chemistry.

Organic, Inorganic and Physical chemistry are regarded as the fundamental and basic fields of chemistry. A few topics in physical and inorganic chemistry will be discussed in the present part of the book.

Elements and Compounds. All the chemical substances may be divided into two categories : **elements** and **compounds**.

Elements are basic units of matter which cannot be decomposed further by any method, chemical or physical.

Compounds are substances formed by the union of two or more elements as the result of a chemical reaction. They cannot be decomposed into constituents by ordinary chemical methods.

Although there are hundreds and thousands of compounds known, the number of elements known is only 103*.

Carbon, oxygen, hydrogen, nitrogen, iron, gold, copper, are examples of elements.

Water, carbon dioxide, copper sulphate, iron oxide, calcium carbonate, are examples of compounds as they are 'built' of hydrogen and oxygen; carbon and oxygen; copper, sulphur and oxygen; iron and oxygen; calcium, carbon and oxygen, respectively.

The distribution of elements in nature is by no means uniform. Some of the elements occur in much more abundance than others. It has been estimated that eight elements, namely, oxygen, silicon, aluminium, iron, calcium, sodium, potassium, and magnesium, make up nearly 97 per cent of the matter in the shell of the earth. The remaining 3 per cent of the earth is composed of all the other elements. The most abundant element in the earth's crust is oxygen. Silicon comes next.

The Laws of Chemical Combination. There are four fundamental laws of chemical combination which were enunciated as a result of numerous experiments, towards the close of the eighteenth and the beginning of the nineteenth century.

1. The Law of Conservation of Mass. This law, put forward by Lavoisier in 1774, states :

The total mass of a reacting system is unchanged as the result of a chemical reaction.

Thus, there can be no loss or gain of weight accompanying a chemical reaction. In more general terms, the law states that *matter can neither be created nor destroyed*. Recent theoretical and practical advances, particularly in the development of atomic energy, have revealed that under certain conditions mass may be converted into energy and *vice versa*. This conversion takes place in accordance with the equation,

$$E = mc^2$$

where m is the mass converted into energy E and c is the velocity of light.

2. The Law of Definite Proportions. The law established by Prout in 1799 may be stated as :

A given chemical compound always contains the same elements combined together in the same proportion by weight.

For example, water from any source always contains 1.008 parts by weight of hydrogen and 8.000 parts by weight of oxygen. Similarly, pure carbon dioxide obtained from any source always contains 12 parts of carbon and 32 parts of oxygen by weight.

*Two more elements of atomic number 104 and 105 have been prepared. Their names have not yet been reported.

The Law of Multiple Proportions. This law discovered by John Dalton in 1804 may be stated as :

If two elements, say A and B, combine to form more than one compound, then different weights of A which combine with a definite weight of B, bear a simple whole number ratio to one another.

The law may be illustrated with reference to the five oxides of nitrogen given in Table 1.1.

TABLE 1.1
Law of Multiple Proportions and Oxides of Nitrogen

Compound	Formula	Relative weights of nitrogen and oxygen			
		Nitrogen	Oxygen	Nitrogen	Oxygen
Nitrous oxide	N_2O	28	16	28	16×1
Nitric oxide	NO	14	16	28	16×2
Nitrogen trioxide	N_2O_3	28	48	28	16×3
Nitrogen tetroxide	N_2O_4	28	64	28	16×4
Nitrogen pentoxide	N_2O_5	28	80	28	16×5

It is evident that different weights of oxygen which combine with a definite weight of nitrogen, bear a simple ratio to one another. The simple ratio is 1 : 2 : 3 : 4 : 5.

4. The Law of Combining Weights. This law established by the experimental work of Richter in 1792-94 may be stated as :

When two or more elements combine with a constant weight of third in certain proportions, they combine with each other in the same proportions or in multiples of these proportions.

For example, 12 grams of carbon combine with 4 grams of hydrogen to form methane (CH_4) and with 32 grams of oxygen to form carbon dioxide (CO_2). Therefore, when hydrogen and oxygen combine they should do so in the proportion 4 : 32, that is, 1 : 8 as they actually do in water (H_2O).

Similarly, 12 grams of carbon combine with 64 grams of sulphur to form carbon disulphide (CS_2) and with 32 grams of oxygen to form carbon dioxide (CO_2). Therefore, when sulphur and oxygen combine they should do so in the proportion 64 : 32, that is, 2 : 1 or in simple multiple of it. Sulphur and oxygen combine in the proportion 1 : 1 in sulphur dioxide which is a simple multiple of 2 : 1.

Dalton's Atomic Hypothesis. John Dalton, an English school teacher (1766-1844) in an attempt to explain the laws of definite composition and multiple proportions, proposed an atomic hypothesis in 1809.

Subsequently, it was found that it could explain all the four laws of chemical combination and so it began to be referred as **atomic theory** rather than as atomic hypothesis.

The postulates of Dalton's atomic theory may be stated as :

1. Matter is composed of small, definite and *indestructible* particles called *atoms*, which are *indivisible*.
2. All atoms of the same element are *equal in weight* and *similar in all respects*. Atoms of different elements differ in all respects.
3. Compounds are formed by the union of atoms of different elements *in simple numerical proportions* such as 1 : 1, 1 : 2, 1 : 3, 2 : 3, etc.
4. The combining weights of the elements are really the combining weights of the atoms.

Although we now know that atom is *not* indivisible and that all atoms of the same element are *not* alike in weight, yet Dalton's atomic theory was the first attempt to organise scientific thinking in chemistry.

Combining Weights or Equivalent Weights. The law of combining weights has given rise to the idea of *combining weights* or *equivalent weights* of elements defined as *that weight of element which combines with or displaces from combination 8.00 parts by weight of oxygen*. Previously, the equivalent weight was defined with reference to 1.008 parts by weight of hydrogen. But now oxygen is preferred, since most of the elements can form compounds more readily with oxygen than with hydrogen.

Sometimes, one and the same element may combine with oxygen to form more than one compound as shown under the law of multiple proportions. In such cases the element will have more than one equivalent weights. For example, the equivalent weight of carbon is 6 in carbon monoxide (CO) and 3 in carbon dioxide (CO₂). The two equivalents bear simple ratio to one another, 1 : 2, as required by the law of combining weights.

Equivalent weights of acids and bases. The equivalent weight of an acid depends upon its basicity and that of a base on its acidity. The *basicity of an acid* is defined as the number of hydrogen ions and the *acidity of a base* as the number of hydroxyl ions which are produced per molecule on ionization. Thus, the basicity of hydrochloric acid which is capable of giving only one H⁺ ion per molecule is one and the basicity of sulphuric acid capable of furnishing two H⁺ ions per molecule is two and so on. Likewise, the acidity of sodium hydroxide capable of yielding only one OH⁻ ion per molecule is one and the acidity of barium hydroxide which can ionise to give two OH⁻ ions per molecule is two and so on.

The *equivalent weight of an acid* is defined as the weight of the acid which gives one H⁺ ion, i.e., 1 part by weight of hydrogen ion, and *equivalent weight of a base* as the weight of the base which gives one OH⁻ ion, i.e., 17 parts by weight of the hydroxyl ion, on ionization.

The relation between the molecular weights and equivalent weights of acids and bases may thus be represented as :

$$\text{Equivalent weight of an acid} = \frac{\text{Its molecular weight}}{\text{Basicity}}$$

$$\text{Equivalent weight of a base} = \frac{\text{Its molecular weight}}{\text{acidity}}$$

Thus,

$$\text{Equivalent weight of HCl} = \frac{\text{Molecular weight}}{1} = 36.5$$

$$\text{Equivalent weight of H}_2\text{SO}_4 = \frac{\text{Molecular weight}}{2} = 49$$

$$\text{Equivalent weight of NaOH} = \frac{\text{Molecular weight}}{1} = 40$$

$$\text{Equivalent weight of Ba(OH)}_2 = \frac{\text{Molecular weight}}{2} = 85.5$$

The equivalent weight of an acid or base expressed in grams is called the **gram equivalent** of the acid or the base.

The *equivalent weight of a base* may also be defined as the weight of the base which is neutralised by one gram equivalent of an acid. This definition helps in the determination of equivalent weights of bases which do not yield OH^- ions directly, e.g., Na_2CO_3 , NaHCO_3 . Since 1 mole of Na_2CO_3 is neutralised by 2 gram equivalents of hydrochloric acid,



the equivalent weight of sodium carbonate is half of its molecular weight.

In the case of NaHCO_3 , 1 mole is neutralised by one gram equivalent of hydrochloric acid,



hence, its equivalent weight is equal to its molecular weight.

Equivalent weights of oxidising and reducing agents. The equivalent weight of an oxidising agent is defined as the weight of the oxidising agent which gives directly or indirectly 8 parts by weight of oxygen. For example, 2 moles of KMnO_4 give on treatment with sulphuric acid 5 gram atoms of oxygen :



In other words, $2(39 + 55 + 64) = 316$ gm. of potassium permanganate give $5 \times 16 = 80$ gm. of oxygen. Hence, weight of KMnO_4 which gives 8 gm. of oxygen = 31.6.

Thus, equivalent weight of $\text{KMnO}_4 = 31.6$

The equivalent weight of a reducing agent is defined as the weight of the reducing agent which takes up 8 parts by weight of oxygen for

its oxidation. For example, two moles of ferrous sulphate require 1 gram atom of oxygen for oxidation :



In other words, $2(56 + 32 + 64) = 304$ gm. of ferrous sulphate are oxidised by 16 gm. of oxygen. Hence, weight of FeSO_4 which takes up 8 gm. of oxygen = 152 (=its molecular weight).

Thus, equivalent weight of $\text{FeSO}_4 = 152$

Equivalent weights of salts. The equivalent weights of salts are evaluated from the equivalent weights of their constituent atoms. The equivalent weights of the atoms are obtained by the expression

$$\text{Equivalent weight} = \frac{\text{Atomic weight}}{\text{Valency}}$$

Thus,

$$\begin{aligned} \text{Equivalent weight of NaCl} &= \text{Eq. wt. of Na} + \text{Eq. wt. of Cl} \\ &= \frac{\text{At. wt. of Na}}{\text{Valency}} + \frac{\text{At. wt. of Cl}}{\text{Valency}} \\ &= \frac{23}{1} + \frac{35.5}{1} = 58.5 \end{aligned}$$

$$\begin{aligned} \text{Equivalent weight of BaCl}_2 &= \text{Eq. wt. of Ba} + \text{Eq. wt. of Cl} \\ &= \frac{\text{At. wt. of Ba}}{\text{Valency}} + \frac{\text{At. wt. of Cl}}{\text{Valency}} \\ &= \frac{137}{2} + \frac{35.5}{1} = 104 \end{aligned}$$

Gay Lussac's Law of Gaseous Volumes. In the same year in which Dalton published his atomic theory (1808), the French chemist, Gay Lussac, discovered that *whenever substances in the gaseous state interact, they do so in volumes which bear simple ratio to one another as well as to the gaseous products formed, provided the volumes are measured under identical conditions of temperature and pressure.* This statement is known as the Law of Gaseous Volumes. For instance, 2 volumes of hydrogen combine with one volume of oxygen to form 2 volumes of water in the form of steam. Similarly, 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrochloric acid gas.

Atoms and Molecules. The exact significance of Gay Lussac's Law was realised by Avogadro, an Italian chemist. The law led him, in the first place, to distinguish between an *atom* and a *molecule*. At that time the word '*atom*' used to describe the smallest conceivable particle of any substance irrespective of the fact whether it is an element or a compound. Avogadro suggested that this term should be restricted to elements only. In addition, he suggested a new term '*molecule*' which

could be used for elements as well as compounds. The two terms were defined as :

An atom is the smallest particle of an element that can take part in a chemical reaction.

A molecule is the smallest particle of an element or a compound that can exist in the free state.

In compounds the molecules consist of two or more different atoms, for example, carbon dioxide (CO_2) molecule consists of one atom of carbon and two atoms of oxygen.

The molecules of elements consist of one or more similar atoms, for example, a molecule of hydrogen consists of two atoms, both of hydrogen.

Avogadro's Law. After distinguishing carefully between an atom and a molecule in 1811, Avogadro enunciated the following generalization in the same year :

Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.

This generalization when first proposed by Avogadro was called Avogadro's hypothesis. But now, as the hypothesis has been proved experimentally, it is termed **Avogadro's law**, and is ranked with other gas laws.

Atomic and Molecular Weights. Since atoms have definite weights as postulated by Dalton and since molecules consist of definite number of atoms, it follows that molecules too have definite and constant weights. The actual weights of atoms and molecules are very small, being of the order of 10^{-23} gram. It is convenient to express these weights with reference to the weight of a standard atom. Oxygen atom is taken as the standard atom*. Thus, atomic and molecular weights are, in reality, *relative weights*.

Atomic weight of an element is defined as the average weight of its atoms relative to the weight of oxygen atom taken as 16.

For example, atomic weight of sodium is 23. This means that each atom of sodium, on average, is 1.4375 times heavier than oxygen atom.

Molecular weight of a substance (element or compound) is defined as the weight of one molecule of the substance relative to the weight of oxygen atom taken as 16.

For example, molecular weight of sulphur dioxide is 64. This means that each molecule of sulphur dioxide is 4 times as heavy as oxygen atom (or twice as heavy as oxygen molecule, O_2).

The molecular weight of a substance is obtained by adding up the atomic weights of all the constituting atoms present in one molecule of the substance. Thus, a molecule of calcium carbonate, CaCO_3 , contains

*Now C^{12} is taken as the standard atom.

one atom of calcium (at. wt.=40), one atom of carbon (at. wt.=12) and three atoms of oxygen (at. wt.=16). The molecular weight of the compound, therefore, is $40+12+48=100$.

The atomic and molecular weights, expressed in grams are termed as **gram atom** or **gram molecule** (or simply as **mole**), respectively.

One mole of any gaseous substance at *N.T.P.* (0°C and 76 cm. pressure) occupies 22.4 litres. This volume is known as **gram molecular volume** or **molar volume**.

Avogadro's Number. *The actual number of molecules present in one mole of a substance* (or in 22.4 litres of a gas at *N.T.P.*) has been determined by a variety of methods. The value known as **Avogadro's number**, is accepted at present as 6.023×10^{23} . Thus, one mole of every substance contains 6.023×10^{23} molecules. Knowing molecular weight of a substance, it is quite easy to calculate the weight of each molecule of the substance. Thus, the weight of each molecule of oxygen is $32 \div 6.023 \times 10^{23} = 5.313 \times 10^{-23}$ gm.

QUESTIONS

1. State and explain the various laws of chemical combination.
2. Define the term equivalent weight. How are the equivalent weights of acids and bases calculated?
3. Define the terms : basicity of an acid and acidity of a base. What will be the equivalent weights of HCl , H_2SO_4 , $\text{Ba}(\text{OH})_2$ and NaOH .
4. Define equivalent weight of (i) an acid (ii) a base (iii) an oxidising agent and (iv) a reducing agent.
Calculate the equivalent weights of H_2SO_4 , NaOH , NaHCO_3 , Na_2CO_3 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, FeSO_4 .
5. Define the terms : Element, compound, atom, molecule, atomic weight, molecular weight, equivalent weight, gram atom, gram mole, gram equivalent.
6. What is meant by Avogadro's number? How would you determine the weight of a single molecule of a substance?

CHAPTER II

PERIODIC CLASSIFICATION OF ELEMENTS

Attempts were made early in the history of development of chemistry as a science, to divide elements into metals and non-metals based on differences in such properties as malleability, lustre, hardness and ability to form acidic or basic oxides. Certain elements such as arsenic and antimony which had properties in common with both metals and non-metals were grouped as metalloids.

With increase in the number of known elements through new discoveries (only 56 elements were known by the middle of last century and today the number has risen to 103*), efforts were made towards a more systematic classification of the elements. The establishment of the atomic theory towards the beginning of the nineteenth century and the development of methods for determining atomic weights soon after, provided a suitable basis for the above classification.

Dobereiner's Triads. Dobereiner in 1830 on careful examination of atomic weights of different elements which were known at that time, showed that there were several groups of three elements each (triads) which had very similar properties and that the atomic weight of the middle element was nearly equal to the arithmetic mean of the atomic weights of the other two elements. Some such triads are shown in Table 2.1.

TABLE 2.1
The Triads

Elements of different triads			Mean atomic weight of the first and third elements
Lithium 7	Sodium 23	Potassium 39	23
Chlorine 35.5	Bromine 80	Iodine 127	81
Calcium 40	Strontium 88	Barium 137	88

*See foot note on page 2.

This regularity was highly surprising and stimulated other workers to discover new triads as well as to extend this rule to new elements as and when they were discovered. But these attempts were not successful.

Further advance in the classification of elements on the basis of their atomic weights had to wait until 1858 by which time atomic weight determinations had been put on a sound basis mainly by the efforts of Cannizzaro.

Law of Octaves. Newlands, an English chemist, in 1866, brought out another regularity amongst the elements known (about 56) at that time. He showed that when the elements (leaving hydrogen) were arranged in the order of increasing atomic weights, every succeeding eighth element had properties similar to those of the first (cf. Table 2.2). On analogy with musical scale, he called this relationship as the law of octaves.

TABLE 2.2
The Octaves

Li 7	Be 9	B 11	C 12	N 14	O 16	F 19
Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.5
K 39	Ca 40					

For example, the eighth element, sodium is very similar to lithium and so is the next eighth occurring element, potassium. The same is true of beryllium, magnesium and calcium; boron and aluminium; carbon and silicon; nitrogen and phosphorus; oxygen and sulphur and fluorine and chlorine.

The chief drawback of the Newland's system was that the regularity broke down after calcium.

Mendeleeff's Table. The most significant contribution towards the classification of elements was made by Mendeleeff in 1869. He arranged the elements in the order of increasing atomic weights leaving blank spaces wherever necessary in such a manner that elements with similar physical and chemical properties were placed in the same vertical column. He concluded, therefore, that *physical and chemical properties of elements are periodic functions of their atomic weights*. This statement is known as the **periodic law** and the table prepared on this basis is known as the **periodic table**.

In the same year, and quite independently, Lothar Meyer, a German chemist, also drew up a comprehensive system of classification based on the atomic weights of elements. He left blank spaces and placed the 56 known elements where their properties fitted them. He predicted that new elements will be discovered to occupy the blank spaces left in the table. But Mendeleeff's table was so clear and the concept was so precise and lucid that his system has formed the basis of even present-day classification of the elements.

MEDELEEFF'S PERIODIC TABLE

MODIFIED AND BROUGHT UP-TO-DATE

ATOMIC WEIGHTS ARE WITH REFERENCE TO $C^{12}=12.0000$

PERIODS	GROUPS															
	IA	IB	IIA	IIIB	IIIA	IIIB	IVA	IVB	VA	VB	VIA	VIB	VIIA	VIIIB	VIII	Zero
First	1 H 1.008															2 He 4.003
Second	3 Li 6.939		4 Be 9.012		5 B 10.811		6 C 12.011		7 N 14.007		8 O 15.999		9 F 18.998			10 Ne 20.183
Third	11 Na 22.990		12 Mg 24.312		13 Al 26.981		14 Si 28.086		15 P 30.974		16 S 32.068		17 Cl 35.453			18 Ar 39.948
Fourth (First long period)	19 K 39.102		20 Ca 40.08		21 Sc 44.956		22 Ti 47.90		23 V 50.42		24 Cr 51.996		25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.71
		29 Cu 63.54	30 Zn 65.38		31 Ga 69.72		32 Ge 72.60		33 As 74.91		34 Se 78.96		35 Br 79.916			36 Kr 83.80
Fifth	37 Rb 85.47		38 Sr 87.62		39 Y 88.905		40 Zr 91.22		41 Nb 92.906		42 Mo 95.94		43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4
		47 Ag 107.87	48 Cd 112.40		49 In 114.82		50 Sn 118.69		51 Sb 121.75		52 Te 127.60		53 I 126.90			54 Xe 131.30
Sixth	55 Cs 132.905		56 Ba 137.34		57 La to 71 Lu		72 Hf 178.6		73 Ta 180.948		74 W 183.85		75 Re 186.20	76 Os 190.2	77 Ir 192.2	78 Pt 195.09
		79 Au 196.967	80 Hg 200.59		81 Tl 204.37		82 Pb 207.19		83 Bi 208.98		84 Po (210)		85 At (216)			86 Rn (222)
Seventh	87 Fr (223)		88 Ra 226.05		89 Ac to 103 Lw											

Lanthanides (Rare earths) The Values in Parentheses are atomic weights of the most stable isotopes

57 La 138.91	58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
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Actinides

89 Ac (227)	90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (239)	95 Am (241)	96 Cm (242)	97 Bk (249)	98 Cf (249)	99 Es (251)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)
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Later researches revealed that *atomic number* and not the atomic weight is the fundamental property of the element. The periodic law has, therefore, been modified as :

The properties of elements are periodic functions of their atomic numbers.

The elements have now been arranged in the order of increasing atomic number instead of increasing atomic weight. In other words, the basis of classification has shifted from atomic weight to atomic number. This has resulted in the removal of a few anomalies of the original Mendeleeff's table. The modified and brought-up-to-date periodic table is annexed in the folder. The inert gases which were not known at the time of Mendeleeff and were discovered in 1894, have been put in a separate group, known as zero group, which is placed either on the extreme left or more commonly on the extreme right of the table.

The atomic weight of each element has been put under the symbol and the atomic number has been put on the top. The vertical columns are called **groups** and the horizontal columns are known as **periods**.

Study of the Table. The Periods. The first period contains two elements, namely, hydrogen and helium. The next two periods consist of eight elements each. Leaving the element of zero group aside, it is evident that the same properties recur in the every eighth element as was first shown by Newlands. The elements of zero group connect the extremely non-metallic (electronegative) elements of group *VII* with the extremely metallic (electropositive) elements of group *I*. Thus, neon connects fluorine and sodium, while argon connects chlorine and potassium, and so on.

The first two elements of the fourth period, potassium and calcium also show recurrence of properties as required by the law of octaves. The difficulty arises after calcium when the law of octaves does not seem to hold good. Mendeleeff overcame this difficulty by postulating correctly the existence of **long periods** consisting of two octaves. Thus, the fourth period is a long period (also called the first long period) consisting of 18 elements. It begins with potassium, an element similar to sodium, and ends with bromine, an element similar to chlorine. The inert element krypton of zero group is the eighteenth element of this period and connects the strongly electro-negative bromine with the strongly electro-positive rubidium of the next period.

The fifth period is also a long period and consists of 18 elements arranged in two rows, the inert element xenon connecting the electro-negative iodine with electro-positive alkali metal cesium of the next period.

The sixth period is also a long period. It consists of 32 elements, out of which 14 elements with atomic numbers 58 to 71 are called **rare earths**. The rare earths are so similar to one another and to lanthanum that they are put together in one place in group *III* beside lanthanum. They are, therefore, now termed as **lanthanides**. If these elements are placed horizontally in the same group, there will be undue sideways

expansion of the table. To avoid this, they are printed as a separate series below the periodic table as shown. The seventh period consists of 17 elements, which include the recently discovered elements obtained artificially by nuclear reactions. As the elements after lanthanum are called lanthanides, similarly the elements after actinium (at. no. 89) are called actinides. To avoid inconvenient sideways expansion of the table, these elements are also printed below the periodic table as shown.

The elements beyond uranium (at. no. 92) have been synthesised artificially by nuclear reactions and are called **transuranic elements**. Their names are neptunium, plutonium, americium, curium, berkelium, californium, einsteinium, fermium, mendelevium, nobelium and lawrencium. They are not known to exist in nature.

The Groups and Sub Groups. The vertical columns constitute groups. Groups *I* to *VII* are divided into two rows of elements. The elements in the first row placed towards the left constitute sub-groups *A* and those in the second row placed towards the right constitute sub-groups *B*. The elements belonging to the same sub-group have similar physical and chemical properties. Thus, lithium, sodium, potassium, rubidium, cesium and francium of sub-group *IA* resemble one another in their physical and chemical characteristics. Similarly, elements, copper, silver and gold belonging to sub-group *IB* have closely related properties.

The elements belonging to two sub-groups of the same group, however, show a marked contrast in their properties. Thus, the elements of the sub-group *IA*, the alkali metals, have strongly electropositive character, form basic oxides, are uniformly monovalent and are soft, silvery-white metals of low density. The elements of the sub-group *IB*, the coinage metals, copper, silver and gold, have much weaker electropositive character, form extremely weak basic oxides and are much harder and denser. Copper and gold also show variable valency.

Uses of Periodic System. The periodic system has proved useful to chemists in a number of ways. It has provided a comprehensive system of classification of the elements which has put the subject of inorganic chemistry on a more rational basis. The study with the help of the periodic table becomes simpler as the properties of the elements can be reasoned out rather than memorised. Knowing the properties of one element in a particular group, those of the other elements belonging to the same group can be anticipated. At the same time the differences in the properties of the elements belonging to different groups can be predicted.

Some of the important uses of the periodic system have been discussed below :

(1) **Prediction of new elements.** With the aid of the periodic system it has been possible to predict the existence of new elements. For instance, when Mendeleeff drew up the periodic table originally, the elements scandium, gallium and germanium had not been discovered. But in order to put similar elements in the same group, Mendeleeff left some

vacant spaces in his table. He also predicted the atomic weights as well as the more important physical and chemical properties of the unknown elements from the positions of the blanks, taking into account the properties of the neighbouring elements. All the three elements were discovered within 10 years of their prediction and in the life-time of Mendeleeff.

Similarly, Mendeleeff had predicted the existence of another element between molybdenum and ruthenium and called it *eka-manganese* as it was expected to lie below manganese in the same sub-group. The element was discovered comparatively recently, in 1947, in nuclear fissions. It is called *technetium* (Tc). Another blank space left by Mendeleeff between tungsten and osmium has been filled by *rhenium* (Re) discovered by Noddack in 1925.

(2) **Correction of atomic weights in doubtful cases.** The periodic system has been useful in correcting atomic weights of some of the elements. For example, when Mendeleeff was preparing his table, beryllium was known to have equivalent weight equal to 4.55 and as its oxide was isomorphous with aluminium oxide, its valency was taken as 3. This gave 13.65 as the atomic weight. With this atomic weight beryllium should have occupied a position between carbon (at. wt. 12) and nitrogen (at. wt. 14). Such a position was so unlikely that Mendeleeff boldly gave a valency of 2 to the element. This reduced the atomic weight to 9.1 and gave it a position in-between lithium (at. wt. 7) and boron (at. wt. 11). This was in keeping with its properties. Later on, the atomic weight of beryllium was found to be 9, *i.e.*, about the same value as suggested by Mendeleeff.

Similarly, the atomic weights of chromium, indium, cerium, etc., were corrected with the help of the periodic table.

(3) **New ideas for research.** The periodic table has also given new ideas to research workers. One such example is the discovery of tetravalent compounds of lead. Formerly, only one tetravalent compound of lead, PbO_2 , was known. But from the position of the element in the same group as carbon, it was surmised that it should be capable of forming other tetravalent compounds also. A careful research led to the preparation of lead tetrachloride, PbCl_4 .

(4) **New ideas in industrial field.** Several light metals have been selected from their position in the periodic table for preparing alloys to be used in automobiles, aircrafts, jet engines, etc.

The development of **freon** (CF_2Cl_2) as a refrigerant is another example of the use of periodic table in industry. The idea arose from realisation of the fact that certain compounds of non-metallic elements of the top of the groups *VIB* to *VIIB* (*e.g.*, C, N, S and F) were highly volatile and could be used as refrigerants. For example, ammonia and sulphur dioxide are good as refrigerants but they are toxic. Careful investigations have led to the discovery of **freon**, a compound of carbon, fluorine and chlorine.

Defects in the periodic Table. The periodic table has a few defects also:

(1) **Position of hydrogen.** The position of hydrogen has been enigmatic. The formation of its typical oxide, H_2O and the production of positive

hydrogen ions (H^+) similar to those of the alkali metal ions (e.g., Na^+ , K^+ , etc.) in the aqueous solutions of their compounds, suggests that it should be placed at the head of the group *IA*. On the other hand, the fact that it exists as a diatomic gas and that with active metals it forms hydrides (e.g., NaH) which in aqueous solution furnish the negative hydride ion (H^-) similar to the halide ions (e.g., F^- , Cl^- , Br^- , etc.) suggests that it should lie at the head of the group *VIIB*.

It is now customary to place hydrogen at the top of group *I* as well as group *VII*.

(2) **Position of lanthanides and actinides.** The lanthanides and actinides cannot be properly included in the periodic table. All the 15 elements of lanthanide series have been put at one place. Same is the case with the 15 members of the actinide series.

(3) **Position of isotopes.** A large number of isotopes of various elements do not find any place in the periodic table.

(4) **Anomalies of the old periodic table.** Mendeleeff's original table was arranged in the order of increasing atomic weights. On this basis, certain pairs of elements such as argon and potassium; tellurium and iodine and cobalt and nickel, would have been placed in groups to which they could not belong from the point of view of their properties. Therefore, their positions had to be interchanged. This led to anomalies.

These anomalies were, however, removed when the elements were arranged in the order of their *atomic number* instead of atomic weight.

(5) **Relative positions of some similar and dissimilar elements.** Certain elements though possessing many dissimilarities have been placed in the same group or even in the same sub-group. Thus, copper, silver, and gold are very much different from alkali metals, yet they have been put in the same group. Similarly, chromium, molybdenum and tungsten are placed in group *VI* along with oxygen and sulphur with which they do not have much in common.

On the other hand, certain pairs of elements having similar properties have been placed in different groups. For instance, copper, silver and gold have a number of properties in common with nickel, platinum and palladium. But the first three are placed in group *I* while the last three fall in group *VIII*. Similarly, iron and chromium resemble aluminium in many respects, but they are placed in different groups.

Improved Periodic Table. Long Form. In order to remove the objection of placing two sets of elements having different properties, in the same group, a new form of periodic table has been drawn. It is shown on page 15. The subgroups *A* and *B* are separated from one another. The *A* sub-groups are arranged on the left while the *B* sub-groups are placed on the right. They are separated by the elements of group *VIII*. The inert gases are located towards the extreme right of the table. In this table, groups of similar elements can be easily located.

Although the periodic system contains a number of irregularities and imperfections, it can yet be regarded as one of the greatest scientific achievements.

IMPROVED PERIODIC TABLE

Long Form

Period	1a	Transitional Elements																7b	Inert gases
I 2 Elements	H 1	2a																	He 2
II 8 Elements	Li 3	Be 4																	Ne 10
III 8 Elements	Na 11	Mg 12																	Ar 18
IV 18 Elements	K 19	Ca 20																	Kr 36
V 18 Elements	Rb 37	Sr 38																	Xe 54
VI 32 Elements	Cs 55	Ba 56	La 57 Lanthanide Series	Lu 71 Lanthanide Series	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
VII 17 Elements	Fr 87	Ra 88	Ac 89 Actinide Series	Lw 103															

Lanthanide Series (Rare earth elements)	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yd 70	Lu 71
Actinide Series	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lw 103

QUESTIONS

1. Write a short account of the historical developments of the periodic classification of elements.
2. Describe briefly the periodic classification of elements. State the advantages and defects of this classification.
3. On what observed relation of the elements was periodic classification of elements based? Mention the advantages and anomalies of this classification and state how these anomalies were explained in the light of modern researches in science.
(Jammu and Kashmir Inter 1959)
4. Mention the advantages and defects of periodic classification of elements.
(Rajputana Inter 1952)
5. Give an account of the periodic classification of elements in the light of the modern work.
(U.P. Board Inter 1955)
6. Explain clearly what you understand by "periodicity in the properties of the elements" in connection with the classification of elements.
(Rajputana Inter 1948)
7. What is meant by Periodic Law? How is the modern Periodic Law different from that of Mendeleeff's? What are 'periods' and 'groups'? The elements of the first short period Li, Be, B, C, N, O, F and Ne have their atomic numbers 3, 4, 5, 6, 7, 8, 9, and 10 respectively. How are the planetary electrons in these elements arranged? What is the gradation of properties in these elements?
(Panjab Inter 1957)
8. Write an essay on the periodic classification of elements. What are the important differences between metals and non-metals?
(Delhi Prep. 1952)
9. Write an essay on the various attempts at the classification of elements leading to the Periodic Table in all its details. State the Periodic Law.
(Delhi Pre-medical 1953)
10. Discuss the periodic classification. Point out its defects and state how these defects have been removed. Describe briefly the Improved Periodic Table.
11. Illustrate with examples the statement that atomic number is a better basis than atomic weight for the classification of elements.
12. Outline briefly the attempts that have been made to classify the elements. What are the main uses of such a classification?
(Jammu and Kashmir Inter 1962)
13. Describe briefly the modern periodic table. What shortcomings still exist in periodic classification?
(Panjab Inter 1961)
14. Explain the terms: Triads, Law of Octaves, Groups, Periods, as applied to periodic classification of elements.

CHAPTER III

2995

STRUCTURE OF THE ATOM

2995-

The Dalton's atomic theory, as has been shown in the first chapter, provides a satisfactory basis for the laws of chemical combination. However, it gives no answer to a number of questions. For instance, it cannot explain why atoms of different elements differ in their weight, valencies, etc. The curious-minded investigators were more or less convinced that *there must be material difference in the 'make up' of the atoms of different elements*. If it were so, atom could not be the ultimate indivisible particle of matter as postulated by Dalton. But there was no evidence to support their conjecture for quite a long time. It was not until many years later that the study of conduction of electricity through gases and development of radio-activity provided evidence to show that *atom is not indivisible but consists of smaller fundamental particles*.

Cathode Rays. The Electron. It was observed in 1880 that when an electric discharge is allowed to pass through a highly evacuated glass tube, the cathode (negative electrode) emits a peculiar radiation (Fig. 3.1.) These radiations, known as the **cathode rays**, travel in



Fig. 3.1. Production of cathode rays.

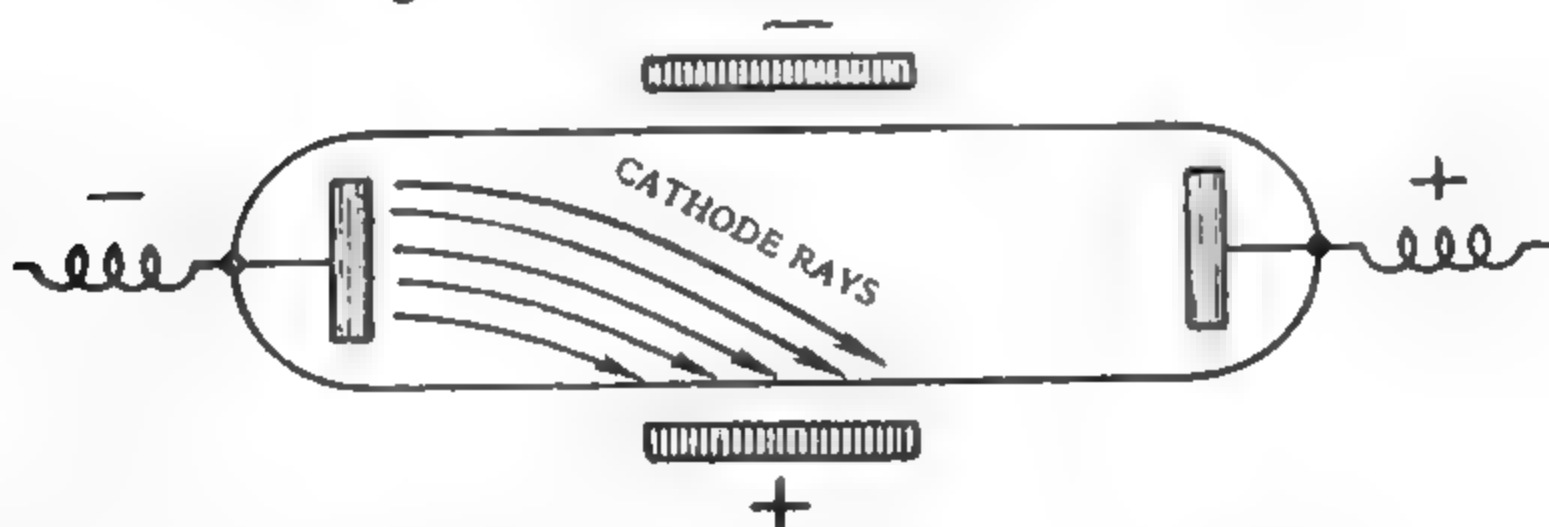


Fig. 3.2. The deflection of cathode rays in an electric field.

straight lines with high speed and cast a shadow of a solid object placed in their path. It was also observed that the rays were deflected in an electric field towards the positively charged plate (Fig. 3.2). This showed that the *rays are negatively charged*.

The rays when allowed to fall on a small pedal wheel caused its rotation. This showed that *the rays consist of material particles*.

In 1897, the English physicist, Sir J.J. Thomson and in 1917, the famous American physicist, Millikan, measured the charge (e) and mass (m) of each particle and found that *these values are identical, irrespective of the nature of the metal forming the cathode or the nature of the gas in the tube*. The most recent work indicates that the charge on each particle is equal to 1.602×10^{-19} coulomb and the mass of each particle is 9.1083×10^{-28} gram, that is, equal to about $\frac{1}{1837}$ of that of the hydrogen atom.

It has been concluded from the above observations that *one common constituent of all varieties of atoms is a negatively charged particle having a mass equal to $\frac{1}{1837}$ of that of the hydrogen atom and charge equal to 1.602×10^{-19} coulombs*. This particle is known as the **electron**.

Since the charge on the electron is the smallest charge of electricity, it is usual to speak of the charge on an electron as *unit negative charge*.

Positive Rays. The Proton. Since electron is an essential constituent of the atom and since the atom, as a whole, is electrically neutral, it follows that there must be some positive electricity, equal in magnitude within the atom. In 1886, Goldstein by careful experiments with discharge tube containing perforated cathode showed the presence of another type of radiation that passed through the holes in the cathode and carried positive charge. These rays are known as **positive rays** or

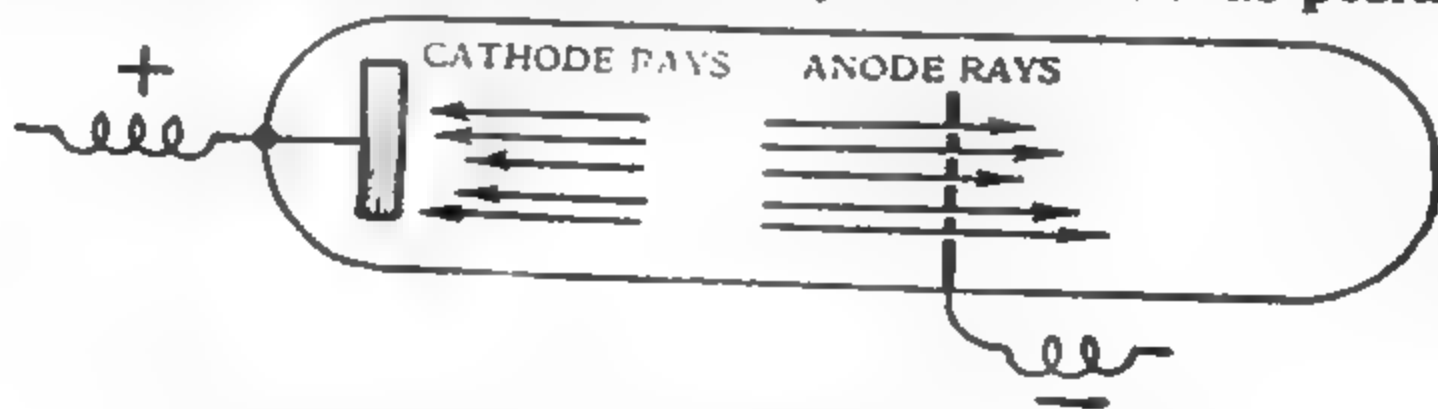


Fig. 3.3. The production of anode rays

anoderays or canal rays (Fig. 3.3). Further studies revealed that *these rays consist of the positive residues of the gas left when one or more electrons are knocked out from the atoms of the gas*. But unlike the electrons, the positive particles are not identical in nature, as the ratio of their charge to mass (e/m) varies with the nature of the gas in the tube.

The hydrogen gas gives the largest value for e/m . This shows that if the charge e is the same in each case, the m mass of the *positive particle* originating from hydrogen is the *lowest*. This has been confirmed by a number of investigators and it is now believed that the *positive particle* given out by hydrogen is one of the *fundamental particles of matter*. Its charge is equal in magnitude but of opposite sign to that of the electron.

Its mass is about 1836 times that of the electron and practically (though not exactly) equal to that of the hydrogen atom. This lightest positive particle is known as proton. The hydrogen atom which is the smallest of all atoms, consists of one proton. The atoms of other elements consist of more than one proton. In fact, the number of protons is different in atoms of different elements, as will be seen shortly. This is the reason why the positive particles constituting the anode rays differ in their masses.

These experiments revealed that the atom consists of (a) negative electrons and (b) positive residues. Further, since the electron has a negligible mass, it follows that *the entire mass of the atom is associated with the positive residue.*

Rutherford's Nuclear Theory. In 1911, Rutherford performed experiments of far reaching importance. He found that when the positively charged α -particles (given out by radium) struck thin metallic sheets, many of them passed through the sheet with no change in their path but some of them were deflected from their original path and quite

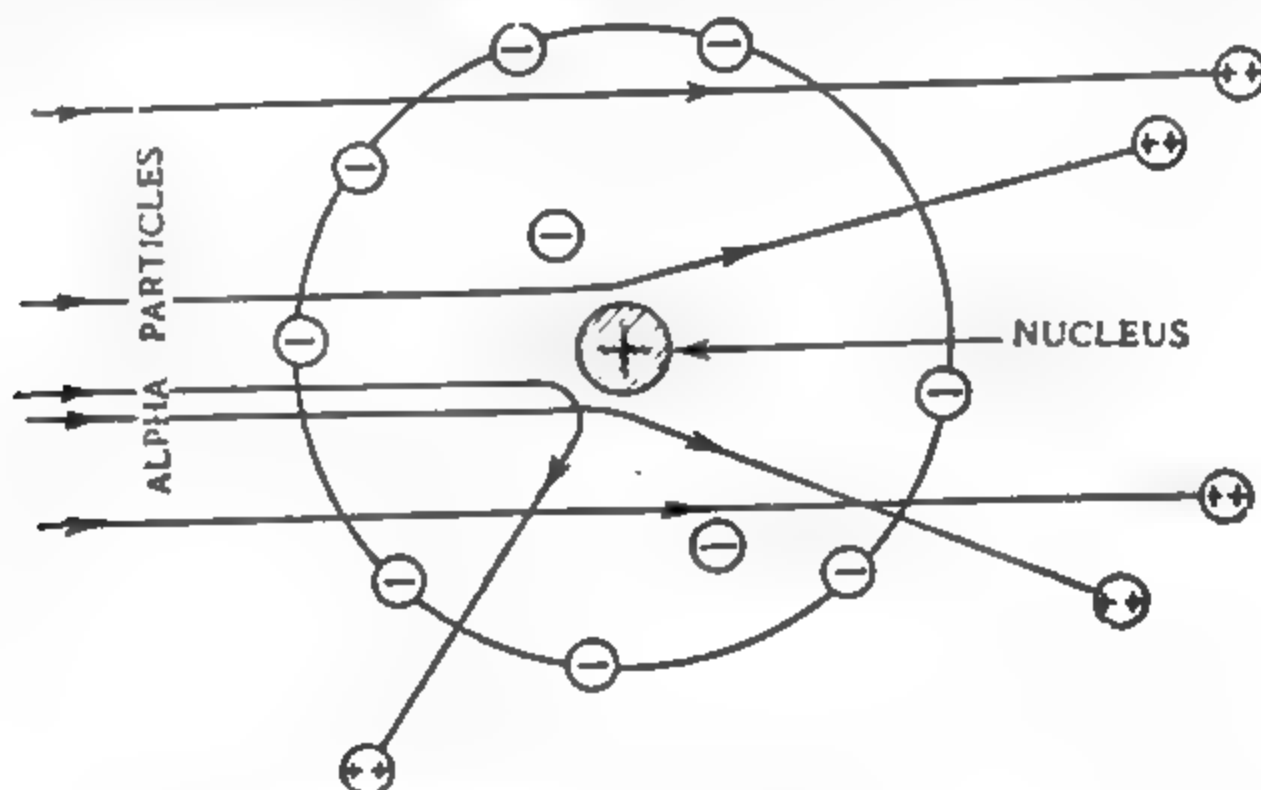


Fig. 3.4. Bombardment of an atom with alpha particles. a few were deflected through 90° or even wider angles (Fig. 3.4). As the α -particles are themselves positively charged and have an appreciable mass (4 times that of the hydrogen atom), their strong deflections showed that *there must be present in each atom a heavy positively charged body.*

On the basis of these experiments, Rutherford put forth his hypothesis of **nuclear atom**. According to this hypothesis, the atom consists of :

(i) An extremely small positively charged body called the **nucleus**, lying at the centre and carrying almost the entire mass of the atom ; and

(ii) A number of small negative electrons, surrounding the nucleus ; the number of electrons being sufficient to balance the charge on the nucleus.

In order to explain why the negative electrons do not fall into the positively charged nucleus on account of their mutual attraction,

Rutherford and later Neils Bohr proposed that the electrons are revolving round the nucleus at high velocities in different shells or orbits. The centrifugal force (tending to take the electrons away from their orbits) balances the force of electrostatic attraction of the positive nucleus for the negative electrons.

This picture of the atom is similar to that of the solar system on a miniature scale. The nucleus represents the sun and the revolving electrons, the planets. The electrons are, therefore, termed as planetary electrons.

Atomic number. Moseley, a young English scientist in 1914, developed a method for determining the number of unit positive charges on the nucleus of an atom. This quantity was called atomic number.

Atomic number of an element is equal to the number of unit positive charges (i.e., the number of protons) on the nucleus.

Since the atom is electrically neutral it follows that the number of positive charges on the nucleus must be equal to the number of planetary electrons. Thus,

$$\begin{aligned}\text{Atomic number} &= \text{Number of positive charges on the nucleus of the atom} \\ &= \text{Number of planetary electrons in the atom}\end{aligned}$$

Subsequent research has shown that atomic number is the most important fundamental characteristic of an atom which determines most of its chemical and physical properties. Therefore, the elements in the periodic table are now arranged *in the order of increasing atomic numbers* and not atomic weights.

The Neutron. By now it should be clear that Rutherford's view of the structure of the neutral atom was that it consists of positive electricity concentrated in a minute nucleus in which also the entire mass of the atom resides, and negative electricity in the form of electrons arranged round the nucleus in different orbits.

Now the atomic number of hydrogen was found by Moseley to be 1. The nucleus of its atom, therefore, should contain one proton. Since the entire weight of an atom is concentrated in its nucleus, the weight of proton is supposed to be very nearly equal to that of the hydrogen atom.

The next element in the periodic table is helium. Its atomic number is 2 and its atomic weight is 4 times that of the hydrogen atom. Therefore, the nucleus of the helium atom must have 4 protons. But since its number is 2, its nucleus must carry only 2 positive charges. Therefore, Rutherford suggested that 4 protons of the nucleus must be associated with 2 electrons so that net positive charge may be 2 units. Thus, the structure assigned to helium atom was as shown in Fig. 3.5. There are 4 protons and 2 electrons in the nucleus and 2 planetary electrons arranged in an orbit around the nucleus.

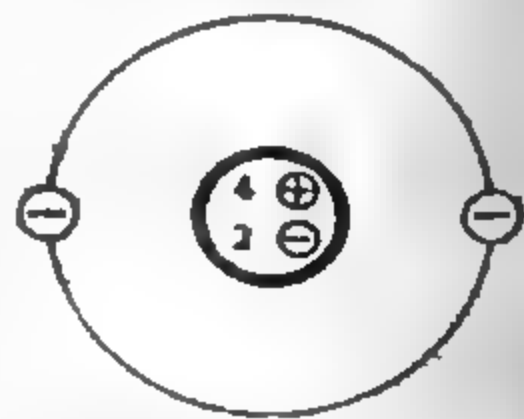


Fig. 3.5. Rutherford's representation of the structure of helium atom.

It was, however, difficult to visualise the existence of free positive and negative electricity so close to each other in the small nucleus.

In 1932, Chadwick discovered that when beryllium or boron is bombarded by alpha particles, *new particles, which carried no charge but had mass equal to that of a hydrogen atom*, were emitted. These particles are called **neutrons**. It is convenient to consider the neutron as a combination of a proton and an electron.

The Structure of the Atom. Before proceeding with a detailed discussion of the structure of the atom, it may be worthwhile to summarise our knowledge of the three fundamental sub-atomic particles. These are (i) *Electrons* (ii) *Protons* and (iii) *Neutrons*.

The **electrons** are negatively charged particles; each electron is regarded as a unit of negative electricity. The electron has a negligible mass equal in magnitude to $\frac{1}{1837}$ of the mass of hydrogen atom.

The **protons** are positively charged particles; each proton is considered as a unit of positive electricity. The mass of each proton is very nearly the same as that of the hydrogen atom. To be more precise, the mass of one proton is equal to 1.0073 on the atomic weight scale.

The **neutrons** are electrically neutral particles having essentially the same mass as that of the proton. The exact mass of neutron is 1.00865 on the atomic weight scale. Each neutron is considered to be composed of one proton and one electron.

Although there are still some uncertain features, it is now generally accepted that the small but massive atomic nucleus consists of protons and neutrons. Since each proton and neutron has a mass approximately 1 (on the atomic weight scale), the atomic weight of an element is approximately equal to the number of protons and neutrons in the nucleus. The net positive charge on the nucleus, that is, the atomic number, is given by the number of protons. To counterbalance the positive charge on the nucleus, there is an equal number of electrons revolving in one or more orbits outside the nucleus. These electrons, as already mentioned, are known as planetary electrons.

Suppose there is an atom of atomic weight A and atomic number Z . Then, evidently, its nucleus consists of Z protons and $A-Z$ neutrons. The number of planetary electrons will be equal to Z . To take a concrete example, lithium has an atomic weight (A) equal to 7 and atomic number (Z) equal to 4. Therefore, its nucleus consists of $7-4=3$ neutrons. Similarly, in the case of sodium :

$$\begin{aligned} \therefore \quad & \text{Atomic weight } (A) = 23 \\ & \text{Atomic number } (Z) = 11 \\ & \text{Number of protons} = 11 \\ & \text{Number of neutrons } (A-Z) = 12 \\ & \text{Number of planetary electrons} = 11 \end{aligned}$$

The number of protons and neutrons in the nucleus and the number of planetary electrons in the orbits, in the case of first 10 elements of the periodic table, are given in Table 3.1.

TABLE 3.1
Atomic Structures

Element	Symbol	Atomic number (Z)	Approximate atomic weight (A)	Nucleus		Orbits
				Protons (Z)	Neutrons (A-Z)	Planetary electrons (Z)
Hydrogen	H	1	1	1	—	1
Helium	He	2	4	2	2	2
Lithium	Li	3	7	3	4	3
Beryllium	Be	4	9	4	5	4
Boron	B	5	11	5	6	5
Carbon	C	6	12	6	6	6
Nitrogen	N	7	14	7	7	7
Oxygen	O	8	16	8	8	8
Fluorine	F	9	19	9	10	9
Neon	Ne	10	20	10	10	10

Other Nuclear Particles. Modern researches have revealed the existence of many other nuclear particles as well. Some of them are mentioned below :

(i) **Positron.** The American physicist, C.D. Anderson, during cosmic ray investigations, in 1932, discovered a new fundamental particle called *positron*. It has the same negligible mass and the same amount of charge as the electron. However, the charge in this case is positive and hence the name *positron*.

(ii) **Meson.** Yukawa in 1935 predicted the existence of another kind of sub-atomic particle, called *meson* (*meso*—middle, Greek) which has a mass in between that of electron and proton. The charge may be positive, negative or zero.

(iii) **Neutrino.** Pauli in 1927 suggested the existence of another new particle, called the *neutrino*. The charge on this particle is zero and mass, though variable, is always less than that of an electron. The free existence of these particles was shown by Allen and Rodeback in 1952.

(iv) **Antiproton.** Segre in 1955 discovered a new particle having mass equal to a proton but with a negative charge. This particle is known as the *antiproton*.

Arrangement of Planetary Electrons. The arrangement of planetary electrons in different shells (or orbits) in the case of first 18 elements (from hydrogen to argon), belonging to first three periods of the periodic table, is based on the following two rules :

(1) *The maximum number of electrons which each orbit can have is given by $2 \times n^2$ where n is the number of the orbit.* Thus, the maximum number of electrons which the orbits 1, 2, 3, 4... can have is given by the expression $2(1^2, 2^2, 3^2, 4^2, \dots)$ or 2, 8, 18, 32..... In other words, the first orbit cannot have more than 2, the second orbit cannot have more than 8, the third orbit cannot have more than 18 and the fourth orbit cannot have more than 32 electrons and so on.

(2) *The maximum number of electrons in the outermost orbit is 8 while the maximum number in the next inner orbit is 18.*

Atomic structures of Hydrogen and Helium. Hydrogen and helium belong to the first period of the periodic table. The atomic number of hydrogen is 1. The atomic weight is also 1. Therefore, the nucleus of

the hydrogen atom consists of one proton. The number of planetary electrons is also one and it must be in the first orbit.

The atomic number of helium is 2 and the atomic weight is 4. Therefore, its nucleus should have 2 protons and 2 neutrons. The number of planetary electrons is 2 and since the first orbit can contain 2 electrons, both the electrons are present in the first orbit. The atomic structures of hydrogen and helium are represented in Fig. 3.6.

Atomic Structures of the Elements of the Second Period.

There are 8 elements, between lithium and neon, belonging to the second period. The first element, lithium, has atomic number 3 and atomic weight 7. Therefore, its nucleus consists of 3 protons and 7 minus 3, that is, 4 neutrons. The number of planetary electrons is 3, two of them arranged in the first orbit and one in the second orbit. The next element, beryllium, has atomic number 4 and atomic weight 9. Therefore, the nucleus consists of 4 protons and 5 neutrons. There are 4 planetary electrons, two in the first orbit and two in the second orbit.

The atomic structures of all the 8 elements of this period are represented in Fig. 3.7. It is seen that the second orbit which begins with

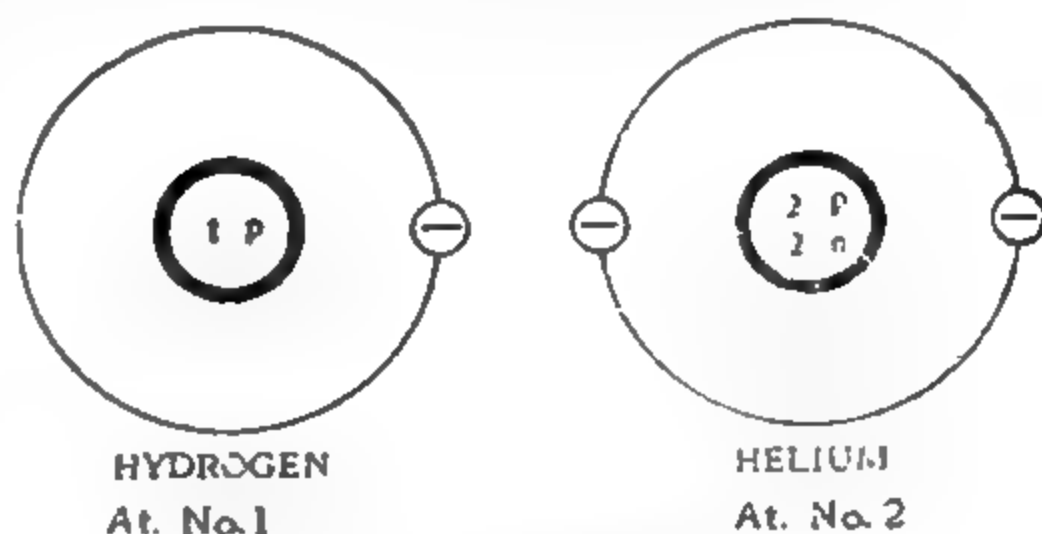


Fig. 3.6. Atomic structures of hydrogen and helium.

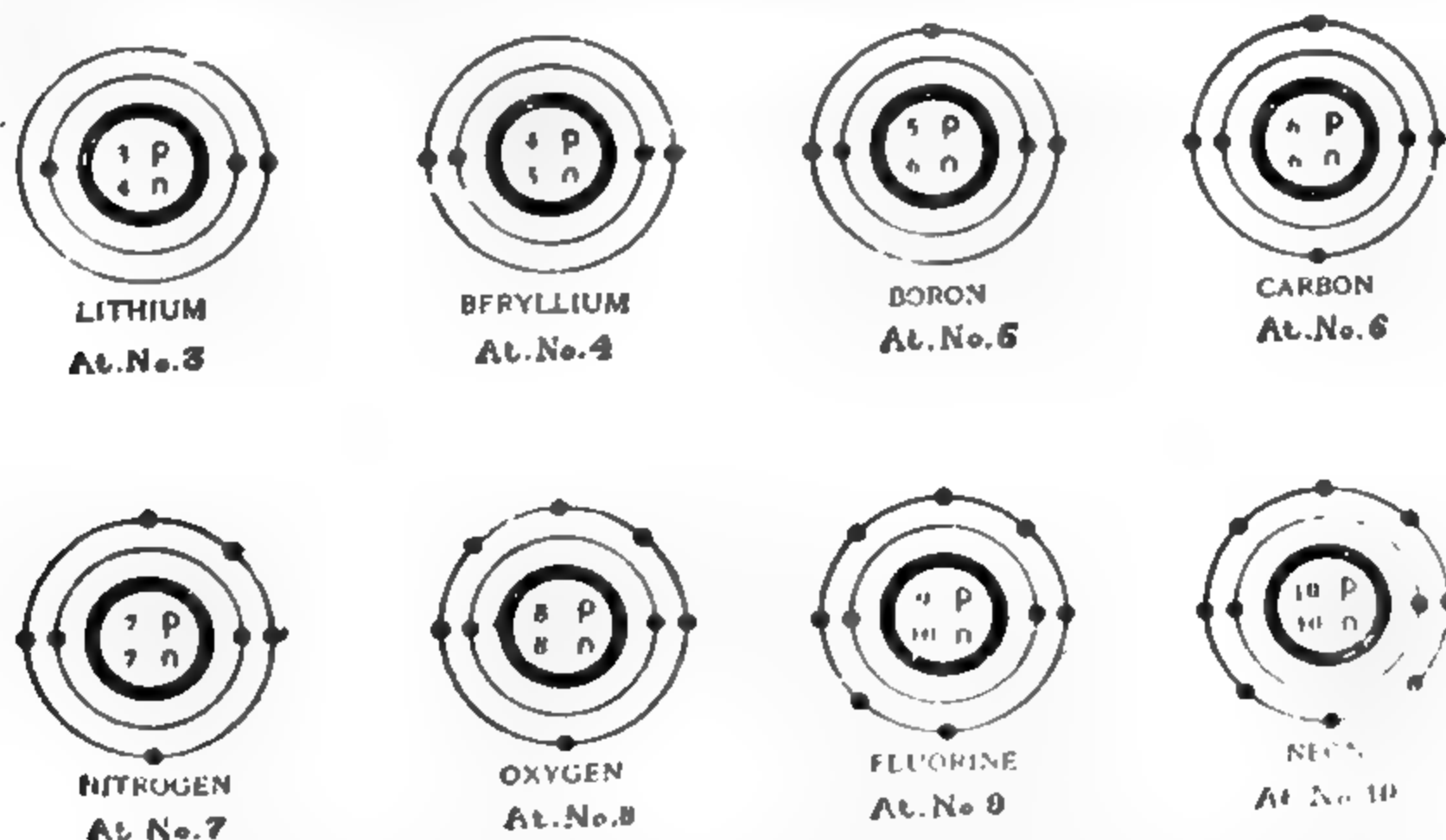


Fig. 3.7. Atomic structures of elements from lithium to neon.

the alkali metal lithium is built up by addition of one electron at a time, as we move to the elements of the next higher atomic number, until

with neon, the number of electrons in this orbit reaches 8, which is the maximum that this shell can have, according to rule (1) given above.

Atomic Structures of the Elements of the Third Period. The third period begins with the alkali metal, sodium, of atomic number 11 and atomic weight 23. Accordingly, there are 11 protons and 12 neutrons in the nucleus. There are 11 planetary electrons : 2 in the first, 8 in the second and 1 in the third orbit. Thus, the third orbit begins with the beginning of the third period. This orbit is completed with the approach of the inert gas, argon, when the number of electrons becomes 8 which is the maximum that this shell, being the outermost, can have according to rule (2) given above.

The atomic structures of the elements of this period are represented in Fig. 3.8.

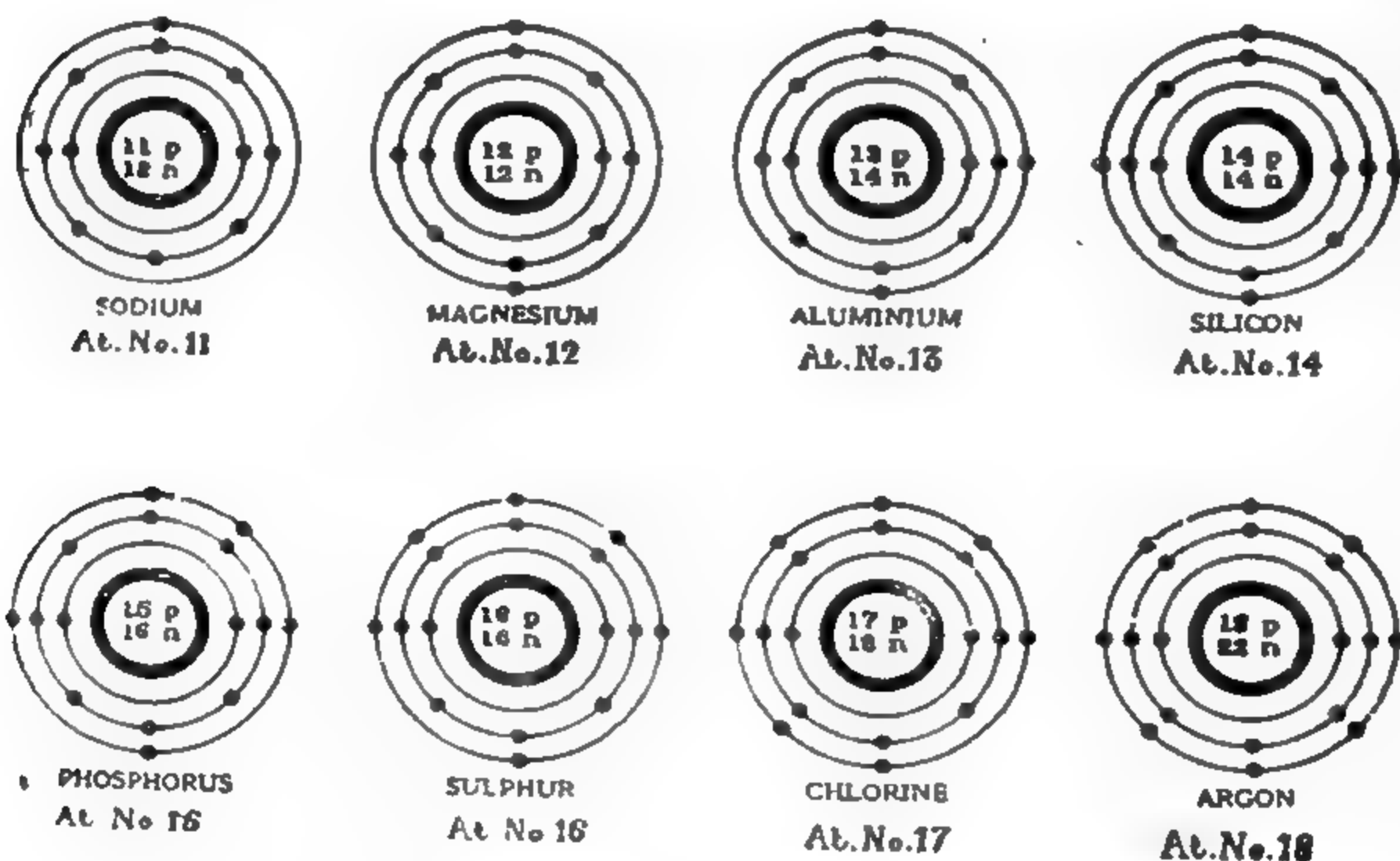


Fig. 3.8. Atomic structures of elements from sodium to argon.

ISOTOPES

It has been stated above that chemical properties of an element depend almost entirely upon its atomic number. Now suppose that the number of neutrons in the nucleus of the atom of an element increases, the number of protons remaining the same. There will be no change in the atomic number of the element and hence no change in its chemical properties or position in the periodic table. The atomic weight, however, will increase. Thus, there will be two kinds of atoms of the same element which will have different weights (mass numbers) but identical chemical properties and identical position in the periodic table. Such atoms are known as isotopes (Greek, *isotopes* : same place).

Isotopes are different kinds of atoms of an element having the same atomic number and same chemical properties and the same position in the periodic table but differing in weight (mass number).

It is now known that most of the elements have two or more isotopes of different weights. The atomic weight of an element is, therefore, defined as the mean of the mass numbers of its different isotopes in the proportion in which they occur. Thus, chlorine has two isotopes of mass numbers 35 and 37 occurring roughly in the proportion 3 : 1. The mean atomic weight of chlorine is, therefore, given by

$$\frac{35 \times 3 + 37}{4} = 35.5$$

It must be emphasised that all isotopes of the same element have the same nuclear charge and the same number of planetary electrons. They differ only in the number of neutrons in the nucleus. The atomic structures of the two isotopes of chlorine are represented in Fig. 3.9.

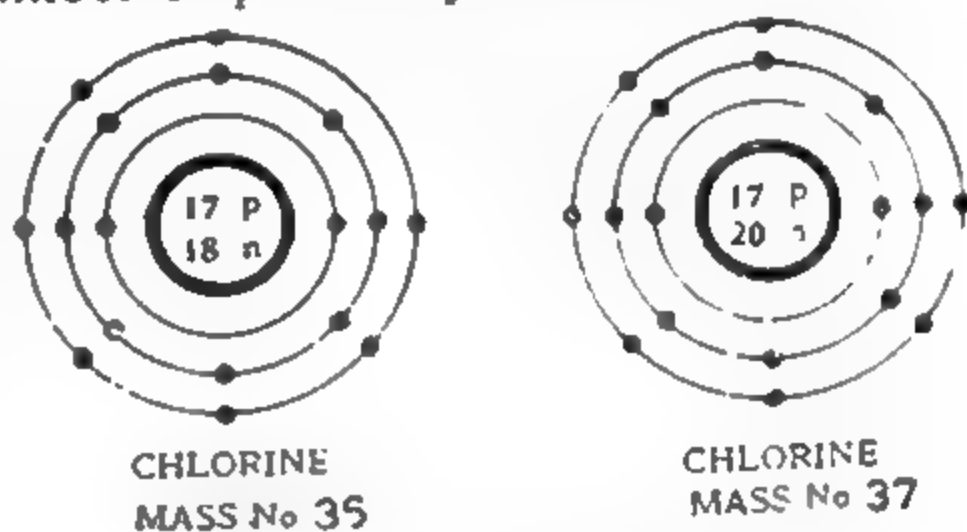


Fig. 3.9. Isotopes of chlorine.

Similarly, hydrogen has three isotopes of mass numbers 1, 2 and 3 represented in Fig. 3.10. These are named as protium, deuterium (heavy hydrogen) and tritium respectively. Hydrogen gas prepared in the laboratory usually consists of 1 part of deuterium for every 6000 parts of protium. Tritium is formed in certain radioactive disintegrations.

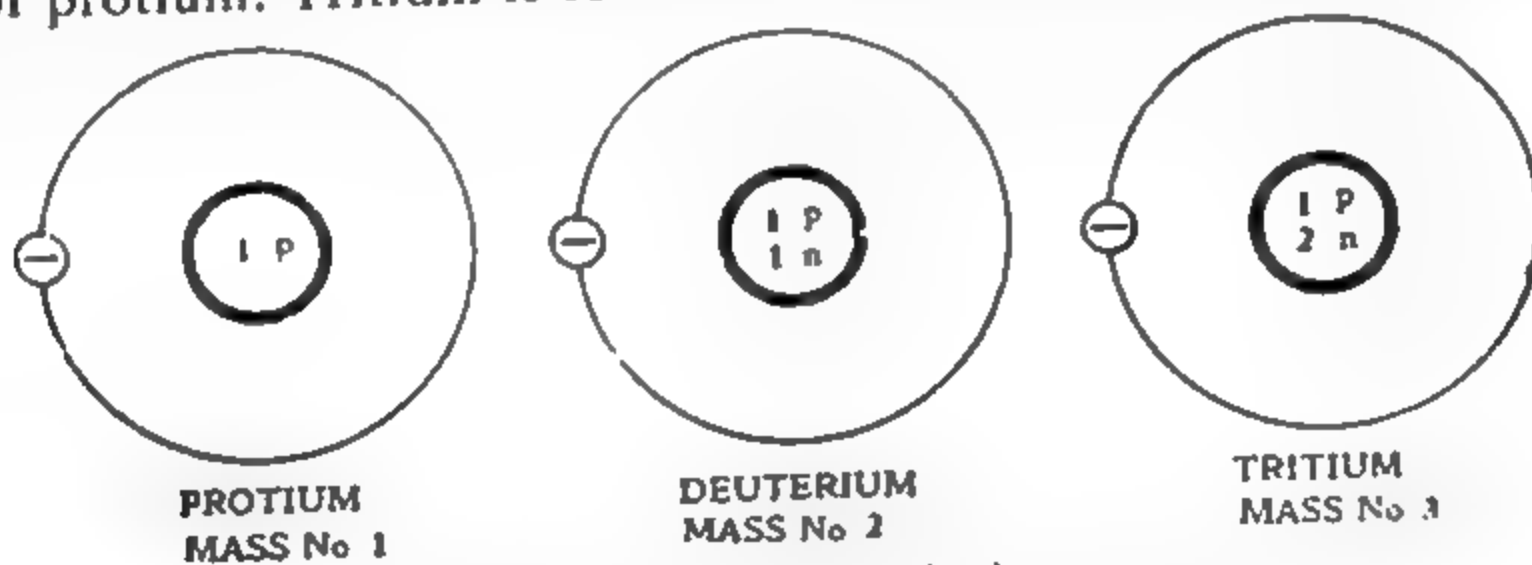


Fig. 3.10. Isotopes of hydrogen.

Argon has two isotopes of mass numbers 39 and 40. In natural argon the second isotope predominates so that the mean atomic weight is 39.94. Similarly, potassium has isotopes of mass numbers 39, 40 and 41. The lightest is most abundant so that the average atomic weight of the element is 39.10.

ISOBARS

As there are so many isotopes, it may happen sometimes that an isotope of one element may have the same mass number as an isotope of another element. Their atomic numbers will be different. For example, argon, potassium and calcium have isotopes of the same mass number 40.

but of atomic numbers 18, 19 and 20. Since their atomic numbers are different, their chemical properties will be different altogether. Such atoms are known as **isobars** (Greek ; *isobars*=same weight).

Isobars are atoms of different elements having the same mass but different atomic numbers.

The atomic structures of isobars of argon, potassium and calcium are given in Fig. 3.11.

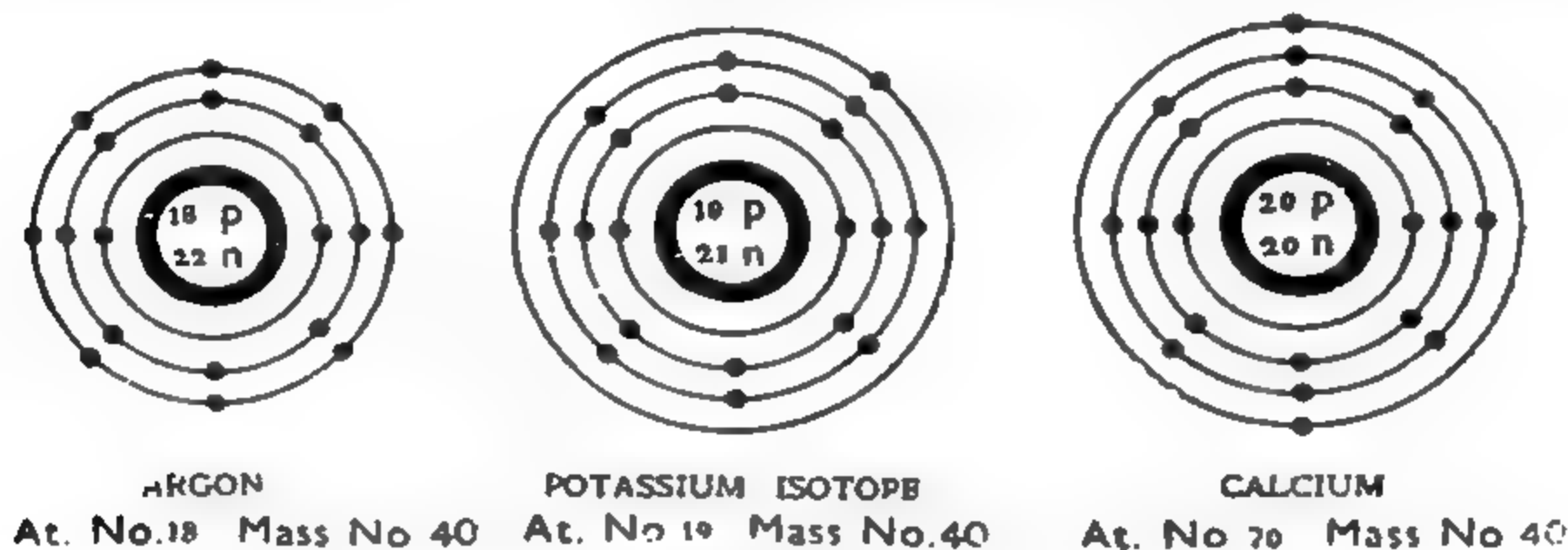


Fig. 3.11. Electronic structure of isobars.

QUESTIONS

- Describe how the discoveries of cathode rays and positive rays have contributed to our knowledge of the structure of the atom.
- Discuss the experimental evidence which led Rutherford to postulate a nuclear atom.
- What is Rutherford's model of the atom? State clearly what you understand by the term 'atomic number'.

4. Give the rules regarding the electronic configurations of the elements of the first three periods. Discuss the electronic configuration of elements with atomic number 2, 6, 12, 16, 18 and 19.

5. What are isotopes? How would you represent the atomic structures of different isotopes of hydrogen with mass numbers 1, 2 and 3 and of chlorine with numbers 35 and 37?

6. What are isobars? How do they differ from isotopes?

7. Explain the terms:

(a) Electron (b) Proton (c) Neutron (d) Atomic number

What are atomic weights, electronic configurations and electrovalencies in the following cases:

(i) 18 neutrons and 17 protons are present in the nucleus of an atom of an element.

(ii) 10 neutrons and 10 protons are present in the nucleus of an atom of an element.

(Punjab Inter 1962)

Ans. (i) 35 ; 2, 8, 7 ; -1 (ii) 20 ; 2, 8 ; zero]

8. What is the modern concept of the structure of an atom? Explain what you understand by neutron, electrovalency and isotope.

The nucleus of an element consists of 9 protons and 10 neutrons. What should be its atomic weight, atomic number and electrovalency?

(Jammu and Kashmir, Inter 1959) (Ans. 19, 9, -1

9. Explain any four of the following terms:

(a) Electron (b) Proton (c) Neutron (d) Nuclear charge (e) Electrovalency (f) Co-valency

Upon what does the mass of an atom depend? Does atomic weight or atomic number determine the chemical properties of an element?

The nucleus of an atom of an element contains 12 neutrons and 11 protons. What is its (i) atomic weight and (ii) electrovalency of the element? Make a guess as to the nature of the element.

(U. P. Board Inter 1961) (Ans. 23, +1)

CHAPTER IV

VALENCY

Historical. Several attempts had been made, since the time of Dalton to explain chemical combination between atoms of different elements to form (molecules of) compounds. Although the laws of chemical combination were known and Dalton's atomic hypothesis had provided an explanation for them, the real cause of chemical combination was not understood. Berzelius, in 1812, proposed a theory of electrostatic attraction. He thought that atoms which combine with one another carried opposite charges. For example, sodium was taken as positively and chlorine as negatively charged, since they combined to give neutral sodium chloride. Frankland and later Kekule, proposed that each element had a definite combining power or valency (Latin, *valentia* means strength). Valency was defined *as the number of atoms of hydrogen with which one atom of an element can combine*. For example, the valency of oxygen was taken as 2 and that of nitrogen as 3, since their compounds with hydrogen, namely, water and ammonia had the composition H_2O and NH_3 , respectively.

These views were later found to be unsatisfactory in explaining the formation of many new compounds which the development of organic chemistry had made possible. Following the publication of Bohr's theory of the arrangement of electrons in different orbits surrounding the positively charged nucleus in an atom in 1913, Kossel and Lewis attempted in 1916 to explain valency in terms of electrons. Sidgewick developed these ideas further and established the modern theory of valency which is also known as *electronic theory of valency*.

The Electronic Theory of Valency. The theory originated when it was realised that the inert gases of the atmosphere which did not participate in any chemical reaction had 8 electrons in their outermost orbit (excepting helium in which there is only one shell and that contains 2 electrons). This led to the idea that the existence of 8 electrons in the outermost shell was in some way connected with the stability of elements. It was, therefore, stated that *when atoms combine to form molecules, a re-arrangement of the electrons takes place in their outermost shells in such a way as to obtain this stable configuration of 8 electrons*. The re-arrangement may take place either (a) by losing or gaining electrons until each atom has an octet or (b) by sharing electrons between the two reacting atoms so that

each atom has an octet. Since combination of atoms takes place by the gain or loss or sharing of the electrons in outermost orbit, they are often called **valency electrons**.

Electrovalent or Ionic Compounds. Electrovalency. When compounds are formed by the transference of one or more electrons from one atom to another, they are called **electrovalent or ionic compounds**.

We may consider the formation of sodium chloride, which is a typical ionic compound. The atomic structures of sodium and chlorine are shown in Fig. 4.1. The thick circles in this figure as well as in subsequent figures represent the nucleus. The arrangement of planetary

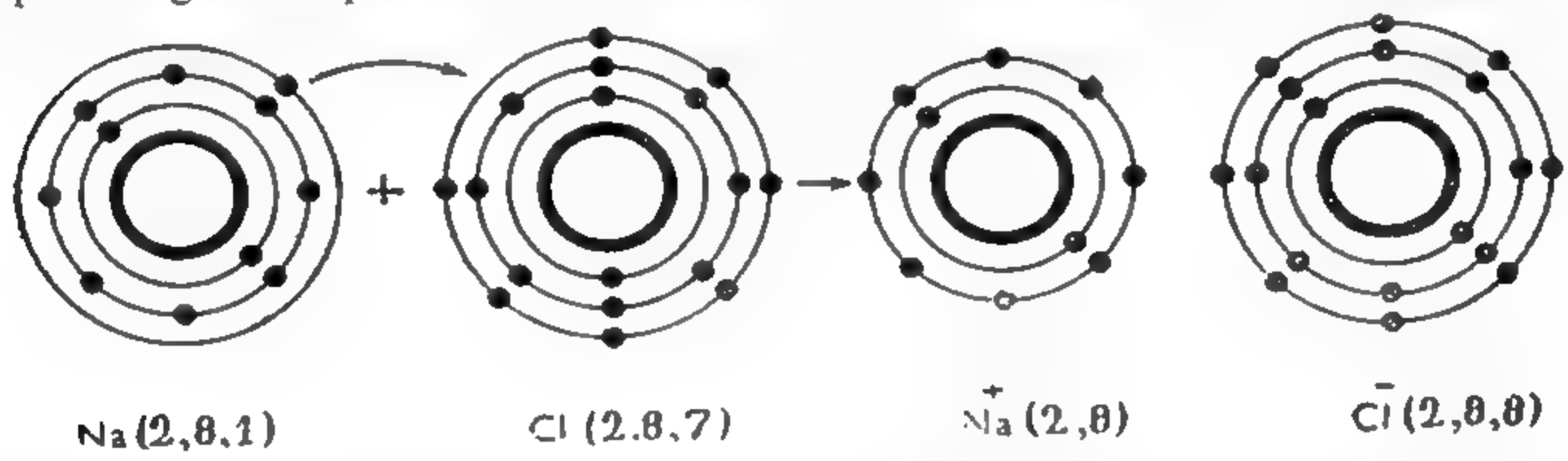


Fig. 4.1. Formation of sodium chloride.

electrons in sodium is 2, 8, 1 and in chlorine 2, 8, 7. The sodium atom gives one electron from its outermost orbit to the chlorine atom. As a result of this transfer, sodium atom has attained the stable octet configuration similar to that of neon (2, 8) and chlorine has attained the stable argon configuration (2, 8, 8), as shown in Fig. 4.1.

But as the sodium atom has given away one electron, it now bears a positive charge and chlorine atom by virtue of the added electron bears a negative charge. These charged particles are called **ions**. Thus, sodium atom changes into a positively charged ion or **cation** and chlorine changes into a negatively charged ion or **anion**. These two oppositely charged ions are held together by forces of electrostatic attraction in the crystal of sodium chloride.

The electron transfer from one atom to another (for example, from sodium to chlorine) is usually represented in a simple manner as shown below. The symbol of the element is written to represent the nucleus as well as the electrons in all shells except the outer-most. The dots (.) or crosses (×) are then put around the symbol to represent the electrons in the outer-most shell. The charge on each ion is represented by the (+) or (-) sign. For example,



This form of chemical combination involving the transference of electrons from one atom to another and leading to the formation of oppositely charged ions which are held together by electrostatic attraction, is known as **electrovalent or ionic linkage** and the valency exhibited is known as **electrovalency**.

For example, in the above case, the sodium atom gives up one electron and chlorine gains one electron. Hence, each atom has an electro-valency of 1. If the atoms of an element lose electrons to form positive ions, the element is said to have a positive valency. Thus, the valency of sodium is +1. Likewise, the elements whose atoms gain electrons to acquire stable configuration are said to have a negative valency. Thus, chlorine has a valency -1.

Formation of calcium fluoride. The formation of calcium fluoride is represented in Fig. 4.2. The electronic configuration of calcium is 2, 8, 8, 2 and that of fluorine is 2, 7. The calcium atom loses two electrons one to each of the two fluorine atoms as shown.

The resulting calcium ion, therefore, carries 2 units of positive charge while each fluorine atom acquires one negative charge.

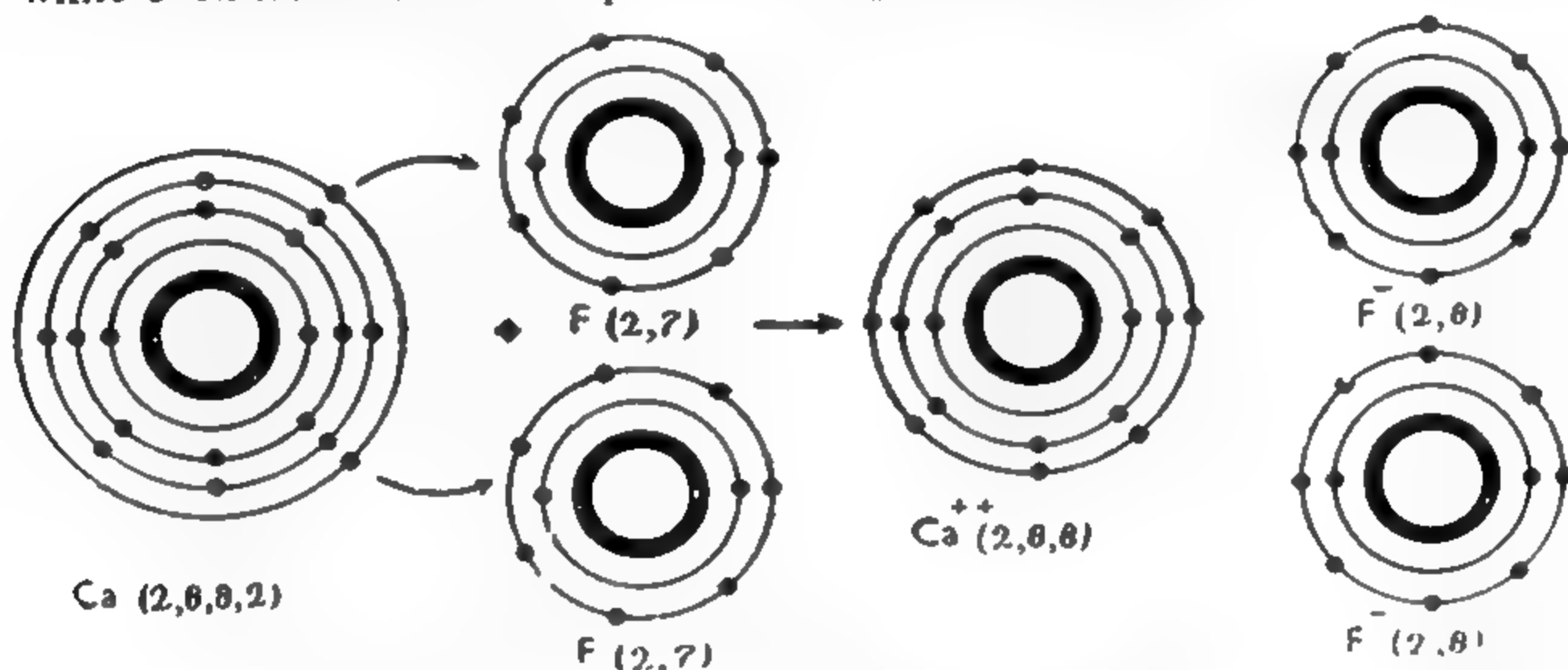


Fig. 4.2. Formation of calcium fluoride.

Formation of magnesium sulphide. Another example is the formation of magnesium sulphide. The atomic structures of magnesium and sulphur are shown in Fig. 4.3. The electronic configuration of magnesium

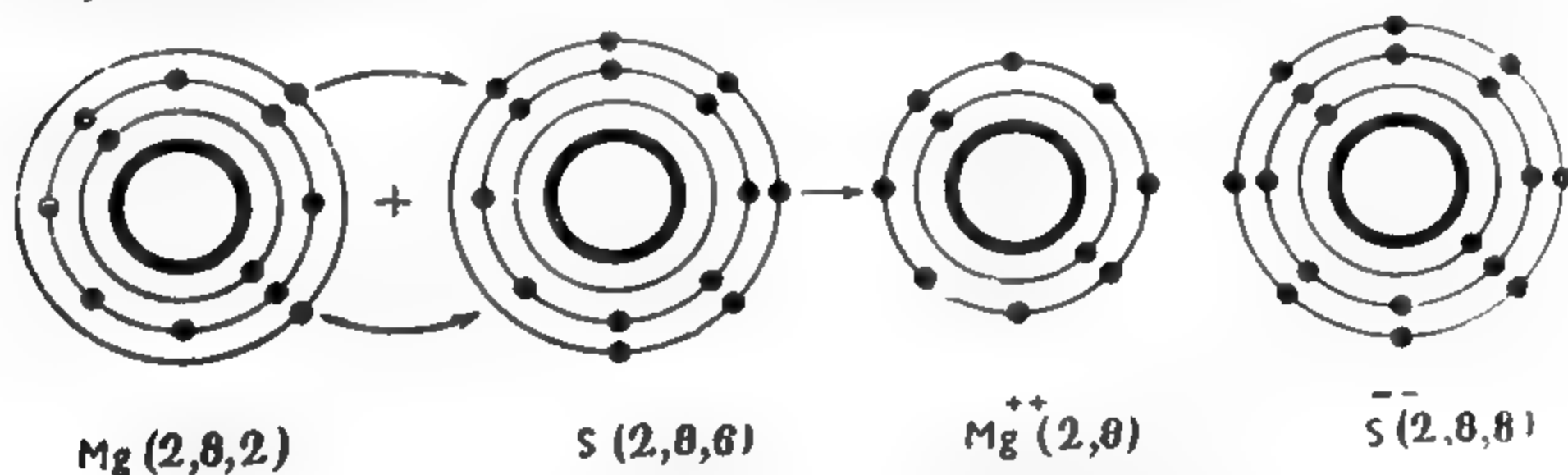


Fig. 4.3. Formation of magnesium sulphide.

is 2, 8, 2 and that of sulphur is 2, 8, 6. Each magnesium atom loses 2 electrons to a sulphur atom as shown. Magnesium atom, therefore, acquires the stable configuration of neon (2, 8) while sulphur attains the stable configuration of argon (2, 8, 8). Thus, we have a doubly positively charged magnesium ion and a doubly negatively charged sulphide ion.

Obviously, the electrovalency of calcium and magnesium is +2 each and that of fluorine and sulphur is -1 and -2, respectively.

Characteristics of electrovalent compounds. The electrovalent compounds possess the following characteristic properties :

1. The X-ray analysis of the crystals of these compounds reveals that they consist of ions (*i.e.*, cations and anions) and not molecules. This confirms that these compounds are formed by the transference of electrons from atoms of one element to those of the other.

2. These compounds, on account of the presence of ions, conduct electricity even in fused state.

3. The compounds are freely soluble in water and other liquids of high dielectric constant. The solution is a good conductor of electricity.

4. The compounds, as a rule, are only slightly soluble in organic solvents.

5. The melting points and boiling points of these compounds are high.

Covalent Compounds. Covalency. There are a large number of compounds whose properties are different from those mentioned above. They do not conduct electricity, for instance, even when dissolved in water. These compounds, therefore, cannot come into existence by the transference of electrons. It was suggested by G. N. Lewis, an American chemist, in 1916, that *atoms may also combine by sharing of the electrons in their outer-most orbits to complete their respective octets*. The shared electrons contribute towards the stability of both the atoms. This type of linkage is known as **covalent linkage** or **covalent bond**. The compounds formed by this mechanism are called **covalent compounds**. Since electrons are not transferred from one atom to another, in this mode of linkage, no charge develops on any of the atoms. Consequently, no ions are formed. Covalent linkage is, therefore, described as **non-ionic linkage**.

A few examples of covalent linkages are given below :

(i) **Formation of hydrogen molecule.** Hydrogen molecule is formed by the union of two atoms. Each atom has one electron in its outermost orbit (the only orbit). It requires one more electron to give it a stable configuration of helium atom. This is achieved by mutual sharing of one electron by each atom as represented below :



Hydrogen atoms

Hydrogen molecule

Thus, each atom has 2 electrons, the maximum number that it needs in the outer orbit. If a pair of electrons shared between two atoms is represented by a single line or bond between them. For example, hydrogen molecule may be represented as H-H.

(ii) **Formation of chlorine molecule.** Each chlorine atom has 7 electrons in its outermost orbit. Each atom shares one of its electrons with the other atom. In other words, two electrons are held in common between the atoms, as shown below :

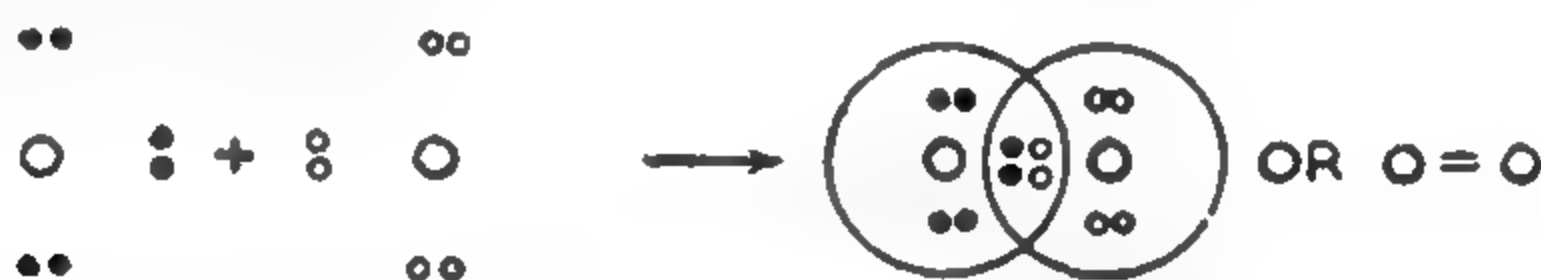


Chlorine atoms

Chlorine molecule

Thus, each atom has its octet completed.

(iii) **Formation of oxygen molecule.** Oxygen atom has 6 electrons in its outermost orbit. Therefore, in the formation of oxygen molecule, O_2 , two of the electrons of each atom are shared between the two oxygen atoms as shown below :



Oxygen atoms

Oxygen molecule

*This form of chemical combination involving the sharing of electrons between two atoms is known as the **covalent linkage** and the valency exhibited is known as **covalency**.*

The **covalency** of an element is equal to the number of electrons shared by its atoms in order to complete the last orbit. Thus, the covalency of hydrogen and chlorine is 1 and of oxygen is 2, in the above examples.

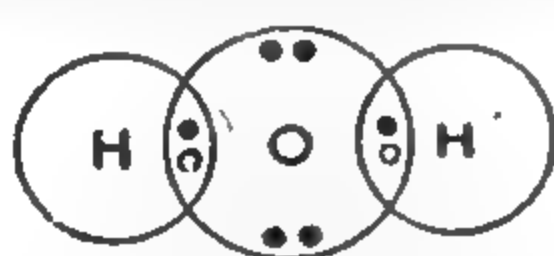
(iv) **Formation of hydrogen chloride.** The formation of hydrogen chloride by the combination of one atom of hydrogen with one atom of chlorine is represented as



Hydrogen chloride

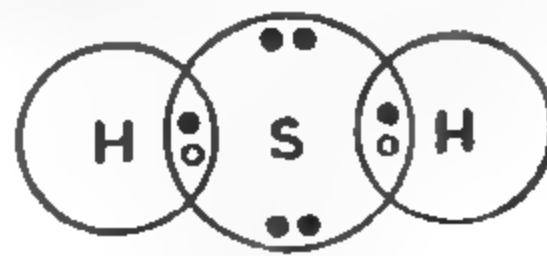
The hydrogen atom acquires stable configuration as in helium [2 electrons in the outermost (first) orbit] and chlorine acquires neon configuration (2,8,8,1).

(v) **Formation of water and hydrogen sulphide.** Oxygen atom has 6 electrons and so has sulphur, in their outermost orbits. These atoms will,



H-O-H

Water

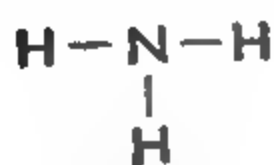
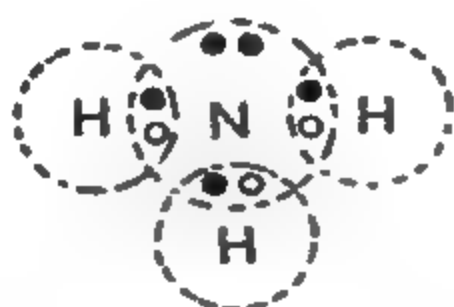


H-S-H

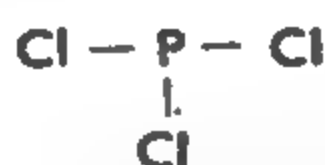
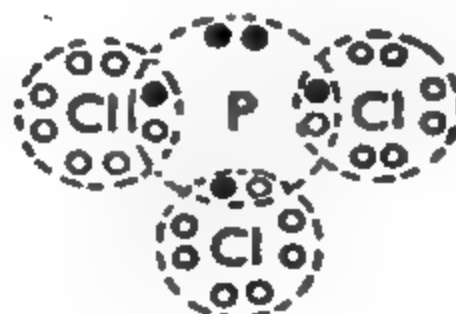
Hydrogen sulphide

therefore, require 2 electrons to complete their octets. In other words, they will form two covalent bonds. This is shown above in the formation of water (H_2O) and hydrogen sulphide (H_2S).

(vi) **Formation of ammonia and phosphorus trichloride.** Nitrogen atom and phosphorus atom each has 5 electrons in the outermost orbit. The formation of ammonia (NH_3) and phosphorus trichloride (PCl_3) is represented as below :



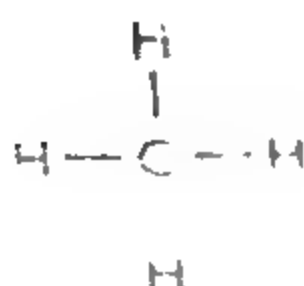
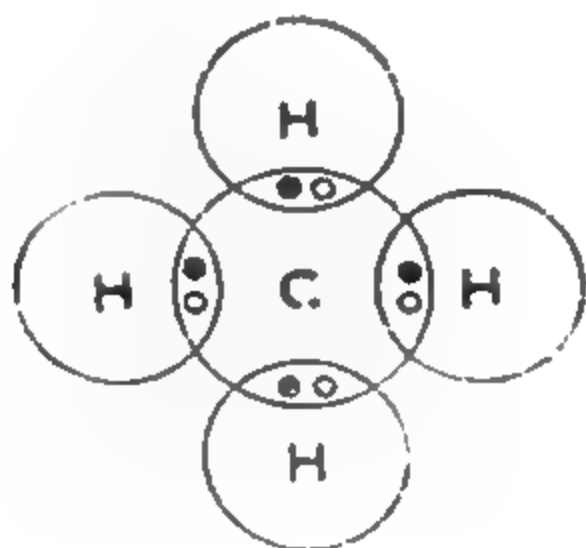
Ammonia



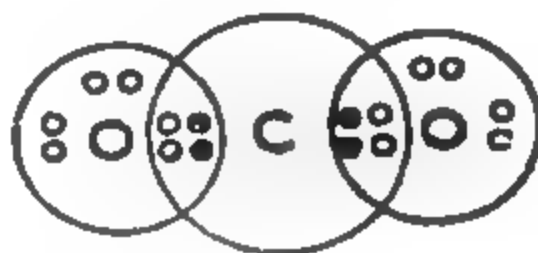
Phosphorus trichloride

Thus, both nitrogen and phosphorus have covalency equal to 3 while hydrogen and chlorine have covalency equal to 1, in these compounds.

(vii) **Formation of methane and carbon dioxide.** Carbon has 4 electrons in its outermost orbit. The formation of methane and carbon dioxide may be represented as :



Methane



Carbon dioxide

Evidently, carbon has a covalency of 4.

Characteristics of covalent compounds. The covalent compounds possess the following characteristic properties :

(1) Since the covalent compounds are formed by the sharing of electrons between the atoms, there is no ion formation. These

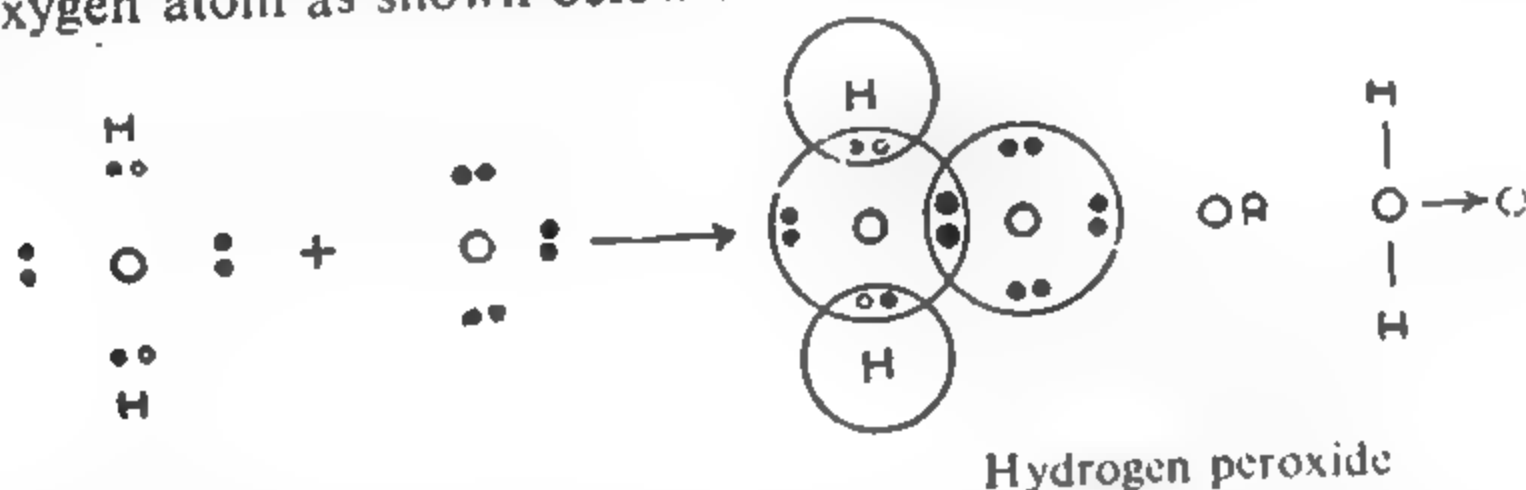
compounds, therefore, exist as molecules, and do not conduct electricity in the fused or dissolved state.

(2) These compounds are generally slightly soluble in water. They are freely soluble in organic solvents.

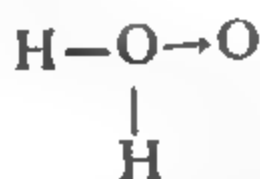
(3) Unlike electrovalent compounds which are generally solids, most of the covalent compounds are gases or liquids with low boiling points. The solid covalent compounds have low melting points.

(4) The covalent bond is rigid and directional, hence there is a possibility of position isomerism and stereo-isomerism among such compounds.

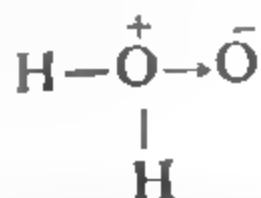
Co-ordinate Linkage and Co-ordinate Compounds. Lewis showed that a different type of covalent linkage can be formed when *both electrons for sharing between the two atoms are contributed by one atom only*. This type of linkage is known as **co-ordinate linkage**. For example, in a molecule of water, the oxygen atom has two pairs of electrons not yet shared with any other atom. In the formation of hydrogen peroxide (H_2O_2) this oxygen atom contributes one of these pairs of electrons to a new oxygen atom as shown below :



The atom which contributes the pair of electrons is known as the **donor** and the atom which accepts these electrons is called the **acceptor**. The free pair of electrons is known as the **lone pair**. In the above example, the oxygen atom in water is the donor whereas the new oxygen atom is the acceptor. This type of linkage is represented by an arrow pointing from the donor to the acceptor. Thus, hydrogen peroxide is represented as



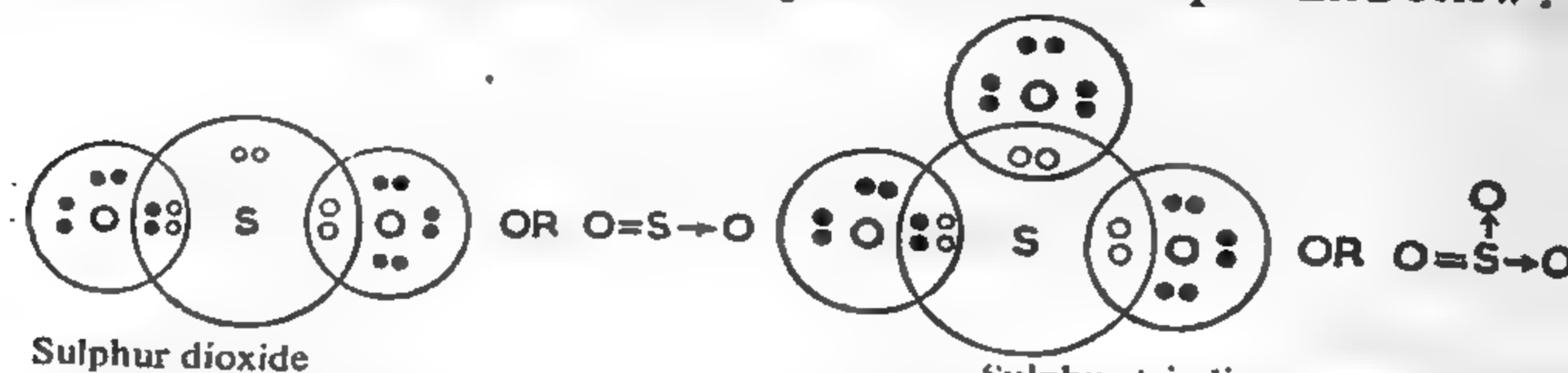
In the formation of this linkage, the first oxygen atom has lost half share of the lone pair of electrons which has been passed on to the second oxygen atom. Thus, there is development of some charge on the two oxygen atoms as shown below :



The donor atom which supplies the electrons becomes positive while the other atom, the acceptor, becomes negative and the molecule acquires

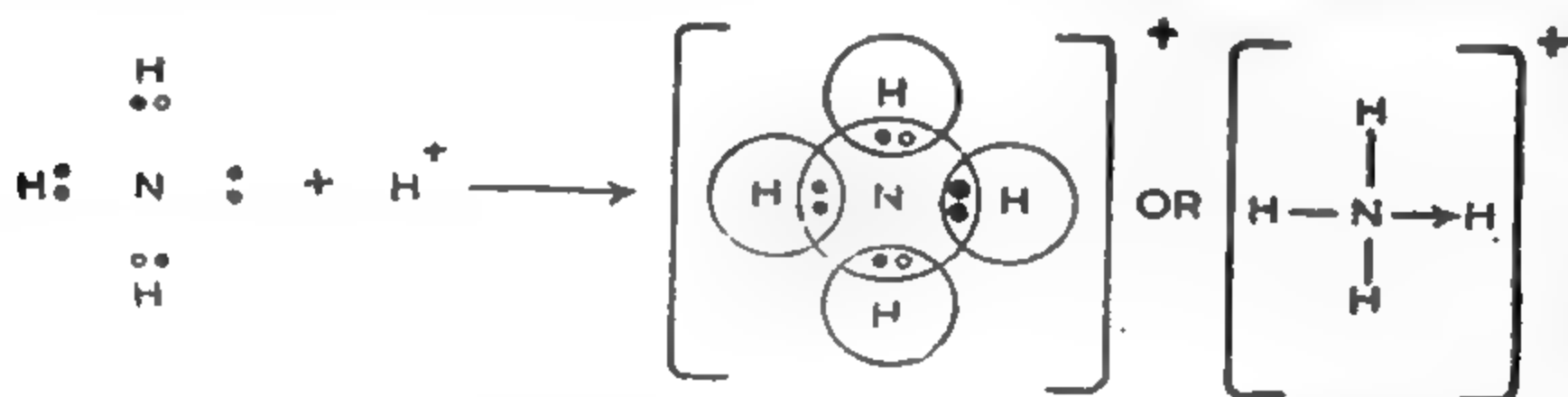
some polarity. The linkage is, therefore, also referred to as a semi-polar linkage.

(i) *Formation of sulphur dioxide and sulphur trioxide.* The formations of sulphur dioxide and sulphur trioxide are represented below :



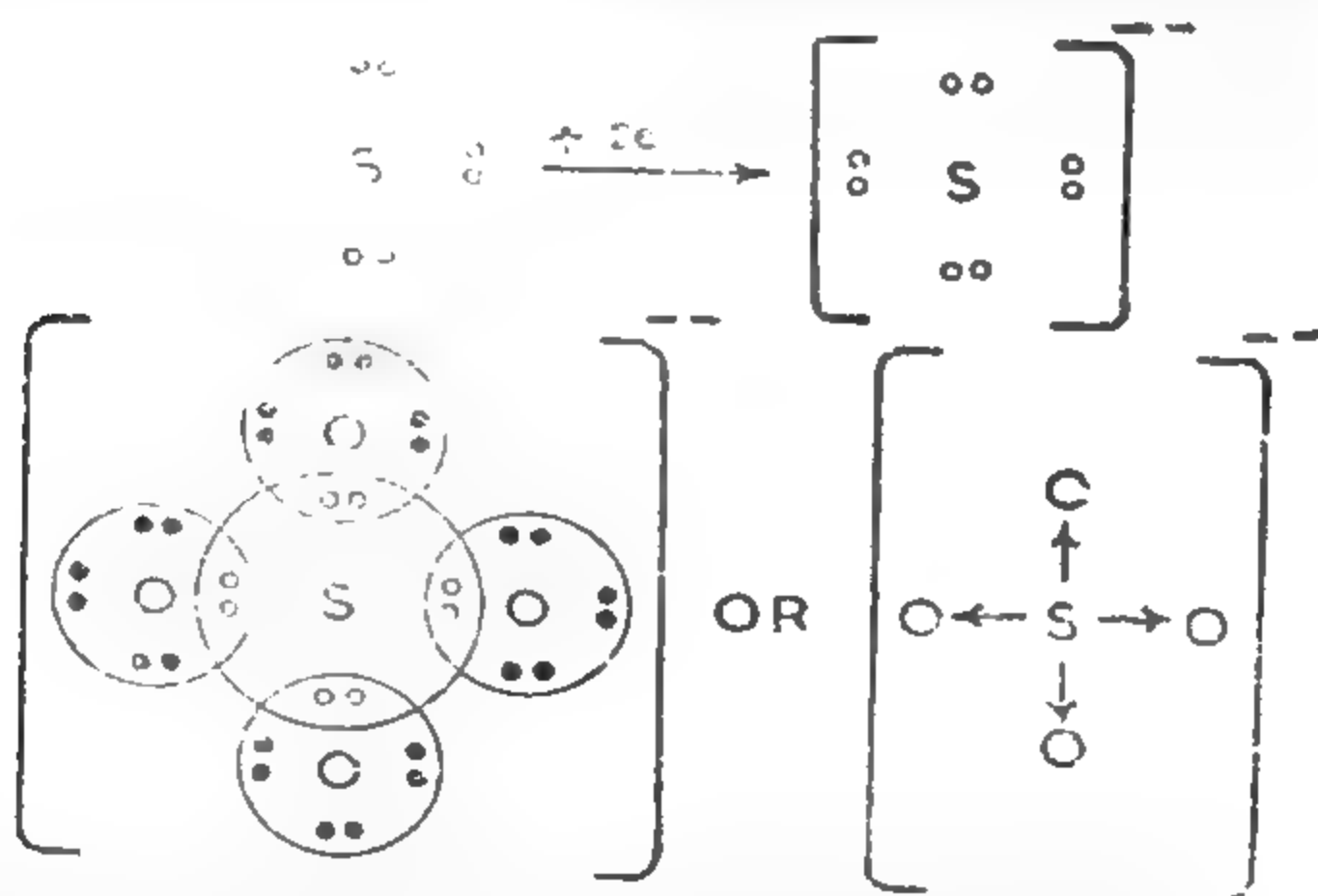
In sulphur trioxide, one oxygen is linked by covalent bond while the remaining two are linked by co-ordinate linkages as shown above.

(ii) *Formation of ammonium ion (NH_4^+).* Ammonium ion is formed by the combination of ammonia with a hydrogen ion (H^+) through a co-ordinate linkage as shown below:



Thus, three hydrogen atoms are attached to nitrogen by covalent bonds, and the fourth by a co-ordinate bond.

(ii) *Formation of sulphate ion (SO_4^{2-}).* The sulphate ion is formed by attaching 4 oxygen atoms to a sulphide ion, by co-ordinate linkages. The sulphide ion carries two negative charges and has its octet complete as shown below :



The sulphide ion possesses 4 lone pairs, which are donated to 4 oxygen atoms, forming the sulphate ion, as represented above.

QUESTIONS

1. Why do atoms combine to form molecules? Give examples.
2. What is meant by stable configuration? Describe the various ways by which an atom may acquire such configuration.
3. Explain what you understand by electrovalency. Describe the important properties of compounds formed by electrovalency.
4. Distinguish clearly between non-ionic and ionic linkage with the help of examples.
5. What are ionic and non-ionic compounds? How do they differ in their properties?
6. What is meant by positive valency and negative valency? Give at least one example of elements or radicals with the following electrovalencies :
+1, +2, +3, and -1, -2 and -3.
7. Discuss the formation of the following compounds :
Lithium chloride, Water, Sulphur dioxide, Barium chloride, Magnesium sulphide, Hydrogen peroxide and Sulphur trioxide.
8. What are electrovalencies in the following cases :
(a) 17 protons are present in the nucleus of an atom of an element.
(b) 11 protons are present in the nucleus of an atom of an element.
9. Explain electrovalency, covalency, and co-ordinate valency. Give the electronic formulae of NaCl and CCl_4 .
10. Write an essay on the electronic theory of valency.
11. Explain with illustration, the following terms :
(a) Covalency (b) Electrovalency
12. Write down the electronic formulae of the following and explain briefly the type of chemical combination they represent :
Hydrogen chloride, Sodium fluoride, Sodium hydride, Magnesium oxide, Methyl chloride, Methane, Carbon dioxide, Chlorine.
13. Write short notes on :
Electrovalency and Covalency. *Jammu & Kashmir T.D.C. (I) 1967*
14. What do you understand by the terms electrovalency and covalency? Elucidate the characteristic properties of electrovalent and covalent compounds. *(Jammu & Kashmir T.D.C. (I) 1966)*

CHAPTER V

CATALYSIS

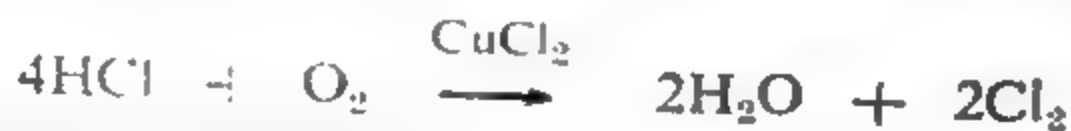
It is a well-known laboratory observation that the decomposition of potassium chlorate takes place much more rapidly and at a much lower temperature, if a little manganese dioxide is added to it. This reaction is written as :



Manganese dioxide is not used up at all and can be recovered unchanged.

A substance that can influence the rate of a chemical reaction but which itself remains unchanged is known as a catalyst and the phenomenon is known as catalysis

This phenomenon has been well-known since the beginning of the nineteenth century, when Thenard found that hydrogen peroxide decomposed more rapidly in the presence of platinum which itself remained unchanged. The term catalysis which means "loosening down" was given by Berzelius in 1835. There are several other examples of catalytic reactions and catalysis. For example, the oxidation of hydrochloric acid gas by atmospheric oxygen takes place more quickly if the gases are passed over cupric chloride.



The combination of hydrogen and oxygen to form water which is slow at ordinary temperature, proceeds more rapidly in the presence of platinum.



Hydrogen peroxide decomposes more rapidly in the presence of colloidal platinum.



Auto-catalysis. In certain reactions, one of the products acts as a catalyst. For example, the oxidation of oxalic acid by acidified potassium

permanganate, represented by the following equation :



increases in velocity as the reaction progresses. This acceleration is due to the presence of manganous ions (Mn^{++}) which are formed in the reaction.

This type of reaction in which one of the products itself acts as a catalyst is known as auto-catalysis.

Promoters. It has been observed in a number of cases that the activity of a catalyst is considerably increased by the addition of a second substance which, by itself, has no catalytic property.

Such a substance which, though not a catalyst by itself, yet promotes the activity of the catalyst to which it is added, is called a promoter.

Thus, molybdenum promotes the catalytic activity of iron in the Haber process for the manufacture of ammonia.



Oxides of aluminium, thorium and uranium also promote the catalytic activity of iron for the above reaction. Copper and tellurium promote the catalytic activity of nickel in the hydrogenation of oils.

Negative Catalysts. In a few cases, a catalyst, instead of speeding up the reaction, may actually retard it. *Such substances are called retarders or negative catalysts or inhibitors.* The negative catalysts are of great use when it is desired to slow down or stop altogether a particular reaction. For example, to slow down the decomposition of hydrogen peroxide, a small amount of acetanilide or glycerine is added. Similarly, to slow the oxidation of sodium sulphite to sodium sulphate by atmospheric oxygen a small amount of ethyl alcohol is added. Lead tetra-ethyl is added to petrol to retard the ignition of petrol vapour on compression in an internal combustion engine and thus to minimise the knocking effect.

General Characteristics of Catalytic Reactions.

1. **The catalyst remains unchanged in amount and chemical composition at the end of the reaction.** The amount of the catalyst found at the end of the reaction is the same as before. However, it may undergo some physical change. For example, manganese dioxide catalyst used in the decomposition of potassium chlorate is found to have changed from granular state to powder form. Similarly, the surface of the platinum gauze used as a catalyst in the combination of hydrogen and oxygen to form water changes from smooth to rough.

2. **Only a small quantity of the catalyst is generally needed.** In many reactions only a small amount of the catalyst is required. For instance, such a low concentration as one gram of colloidal platinum in 10^6

litres can catalyse decomposition of hydrogen peroxide. Similarly, as low a concentration as one gram of cupric ion in 10^9 litres can catalyse the oxidation of sodium sulphite to sodium sulphate by atmospheric oxygen.

3. **The catalyst does not alter the position of equilibrium in a reversible reaction.** A catalyst can only hasten the approach of equilibrium in a reversible reaction. It does not alter the concentrations of the products. For example, in the reaction,



the presence of platinised asbestos (catalyst) causes an appreciable increase in the rate of the reaction and hastens the approach of equilibrium but it does not in any way increase the yield of sulphur trioxide.

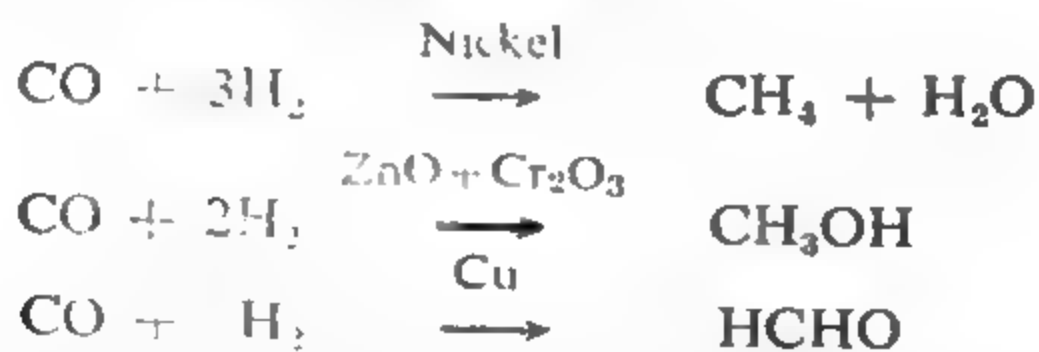
4. **The catalyst does not initiate the reaction.** The reaction is already occurring, though extremely slowly, in the absence of the catalyst. The function of the catalyst seems to be only to speed up the reaction considerably.

5. **The catalyst is specific in its action.** For example, manganese dioxide can catalyse the decomposition of potassium chlorate but not that of potassium perchlorate or potassium nitrate.

However, transitional metals like iron, cobalt, nickel, platinum and palladium can catalyse reactions of various types.

6. **Catalysts cannot alter the nature of the products of the reaction.** The combination of nitrogen and hydrogen under suitable conditions results invariably in the formation of ammonia whether a catalyst is added or not. Similarly, potassium chlorate on decomposition gives potassium chloride and oxygen whether manganese dioxide is added or not.

However, there are a few exceptions. Carbon monoxide and hydrogen combine to form methane or methyl alcohol or formaldehyde depending upon the nature of the catalyst used :



7. **A catalyst is poisoned by certain substances.** It has been found that impurities of any type, even if present in small amounts, inhibit or retard the rate of catalysed reactions to a large extent. These impurities are, therefore, called **catalytic poisons**. For example, the rate of combination of sulphur dioxide and oxygen (in the contact process) is slowed down considerably if some arsenic compounds are present even in traces. Now-a-days, vanadium pentoxide catalyst is preferred because it is much less sensitive to poisoning. Similarly, traces of mercury reduce the catalytic activity of copper for the combination of ethylene and hydrogen to form ethane.

Applications of Catalysis. Catalysis plays an important role in a large variety of laboratory and fermentation reactions.

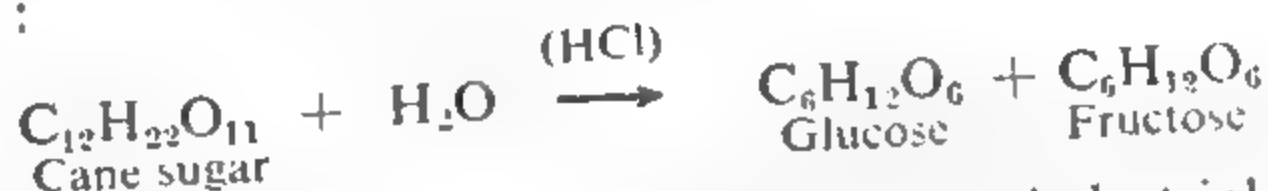
1. Laboratory Reactions. A few typical examples of laboratory reactions are given below :

(a) *Manganese dioxide* is used as a catalyst in the formation of oxygen by heating potassium chlorate.

(b) *Platinum* is used as a catalyst in the combination of hydrogen and oxygen gases to form water vapour.

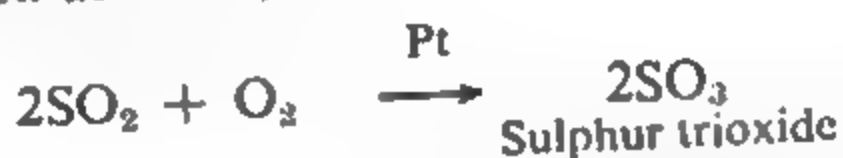
(c) *Colloidal platinum* is used as a catalyst in the decomposition of hydrogen peroxide.

(d) *Hydrogen ions* (dilute acids) are used as catalysts in the inversion of cane-sugar :



2. Industrial Reactions. Some of the important industrial reactions which take place in the presence of catalysts are given below :

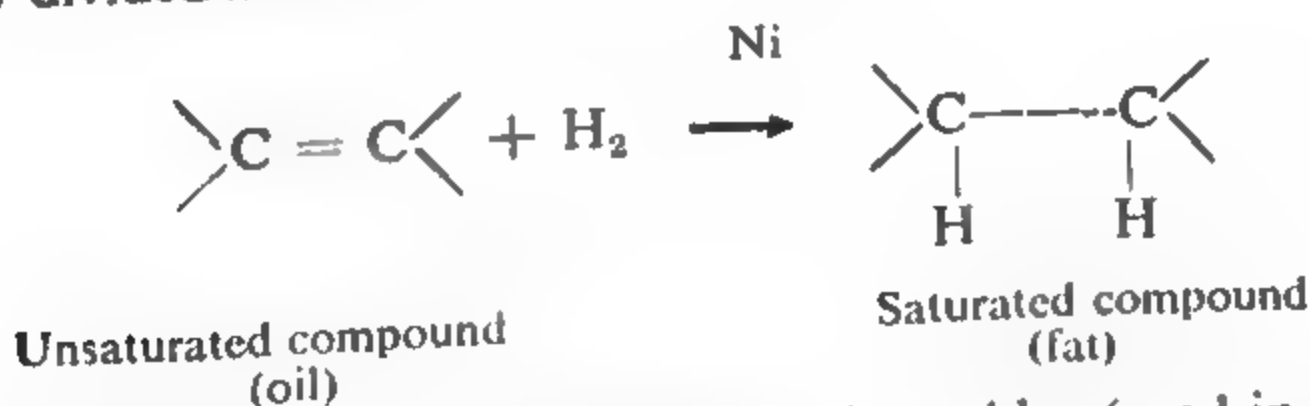
(a) Combination of sulphur dioxide and oxygen in the *contact process* for the manufacture of sulphuric acid is catalysed by platinum deposited on asbestos (*platinised asbestos*) :



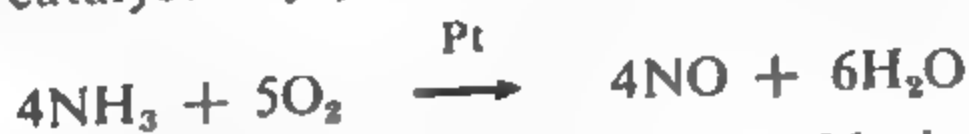
(b) Combination of nitrogen and hydrogen to form ammonia (*Haber process*) is catalysed by *iron* in the presence of *molybdenum* :



(c) Hydrogenation of oils to produce *vanaspati ghee* is catalysed by finely divided *nickel* :



(d) Oxidation of ammonia to nitric oxide (used in the manufacture of nitric acid) is catalysed by *platinum* (*Ostwald's process*) :

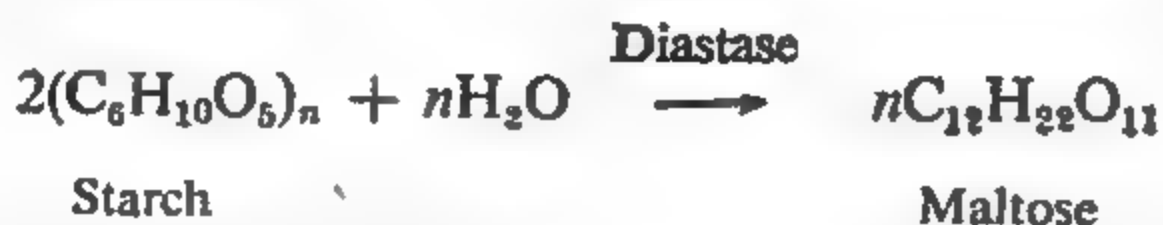


(e) Oxidation of hydrochloric acid gas to chlorine is catalysed by *cupric chloride* (*Deacon's process*) :

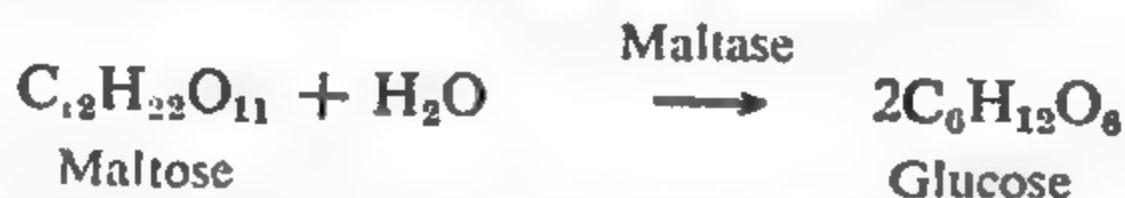


(f) The cracking of kerosene oil is catalysed by certain *silicates*.

3. **Fermentation Reactions.** Some reactions are catalysed by complex organic substances (known as **enzymes**) which are derived from living organisms. Such reactions are called *fermentation reactions*. Each enzyme can catalyse a specific reaction. For example, the enzyme *diastase* produced in the germinated barley seed converts starch into a sugar known as maltose :



Another enzyme called *maltase* converts maltose into glucose :



The enzyme known as *zymase*, produced by living yeast cells, converts glucose into ethyl alcohol :



The enzymes get poisoned by cyanides.

QUESTIONS

1. What is meant by catalysis ? Give examples of this phenomenon.
2. Name a few catalysts. Describe briefly at least one reaction catalysed by each of them.
3. Write notes on :
Auto-catalysis ; Negative catalysts. Promoters. Give examples.
4. What are enzymes ? Why are they regarded as catalysts ? Give some of the reactions catalysed by enzymes.
5. What are general characteristics of catalytic reaction ? Discuss them fully.
6. Give the main industrial processes which require the use of catalysts. Name the catalyst used in each reaction.
7. Describe the use of following substances as catalysts :
(1) Colloidal platinum (2) Platinized asbestos (3) Finely divided nickel
(4) Manganese dioxide (5) Nickel oxide.
8. Write short notes on any two of the following
(i) Catalysts in industry.
(ii) Electrovalency and covalency.
(iii) Electroplating.
(iv) Industrial softening of water.

(Jammu & Kashmir T.D.C. (I) 1967)

CHAPTER VI

SOLUTIONS

Solution. A solution is defined as a *homogeneous mixture of two (or more) substances the composition of which may vary within limits*. The components of a solution are called *solvent* and *solute*. The component which is present in larger proportion is termed the solvent and the component which is present in smaller proportion is called the solute. The term solution is not restricted to any particular physical state of matter. It is possible to have (a) solutions of gases in gases (e.g., air), gases in solids (e.g., hydrogen in palladium) or gases in liquids (e.g., aerated water), (b) solutions of liquids in liquids (e.g., alcohol in water), liquids in solids (e.g., mercury in zinc) and (c) solutions of solids in solids (e.g., brass) or solids in liquids (e.g., sugar in water).

Only the solutions of solids in liquids have been described in the present volume.

The concentration of a solution is expressed either in terms of the number of grams or gram moles of the solute per litre of the solution. In the latter case the strength is referred to as **molarity**. In volumetric work, concentration is often expressed as the number of gram equivalents of solute per litre of solution, when it is referred to as **normality**.

Solutions of Solids in Liquids.

In the case of solutions of solids in liquids, the liquid is invariably referred to as the *solvent* and the solid dissolving in it as the *solute* irrespective of their relative proportions.

Saturated Solution.

If, to a given amount of a solvent maintained at a given temperature a solute is added in increasing amounts, a stage is reached when some of the solute remains undissolved no matter how vigorously the solution is stirred. The solution is then said to be **saturated**. A solution in contact with excess solute is said to be saturated.

Super Saturated Solution.

A solution whose concentration exceeds that of a saturated solution is called a **supersaturated solution**. On heating crystals of sodium

thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, to about 60° in a clean vessel the crystals appear to melt and the salt dissolves in its own water of crystallisation. The amount of sodium thiosulphate in this solution is far in excess of the amount present in a saturated solution obtained on adding the solid to water at the same temperature in the usual manner. If a crystal of sodium thiosulphate is added or if dust is introduced into the solution, the extra amount of the solute is seen to separate out immediately. This shows that a supersaturated solution is only a *metastable* system.

Solubility.

The amount of a solute dissolved in 100 gm of a solvent to form a saturated solution at a given temperature is defined as the solubility of the solute in that solvent at that temperature.

Determination of Solubility. The solubility of a substance in a given solvent at a given temperature is determined as below :

An excess of the solute is shaken with the solvent taken in a flask placed in a thermostat maintained at the required temperature, so as to get a saturated solution. A suitable amount of the saturated solution is withdrawn quickly from the flask with the help of a pipette provided with a plug of cotton-wool or glass wool to check the sucking in of any solid. The pipette is warmed in the thermostat before use in order to avoid any cooling and consequent deposition of the solid in the pipette. The solution is then transferred to a weighed dish which is re-weighed to record the weight of the solution taken. The latter is then *gently evaporated* to complete dryness and the dish is weighed again. From this the weight of the solute in the solution can be evaluated. The solubility is then calculated as below :

Let the weight of the solution = w_1 gm.

Weight of the solute = w_2 gm.

\therefore Weight of solvent in the solution

$$= (w_1 - w_2) \text{ gm.}$$

\therefore Solubility

$$= \frac{w_2 \times 100}{w_1 - w_2} \text{ gm.}$$

The solubilities of some common substances in water, are given in Table 6.1.

TABLE 6.1
Solubilities of Common Substances in Water at 0°C

Substance	Solubility (gm. per 100 gm.)
Sodium chloride	35.7
Ammonium chloride	29.4
Ammonium bromide	68.0
Potassium nitrate	13.3
Aluminium sulphate	31.3
Sodium carbonate	21.5
Sodium bicarbonate	6.9
Sodium nitrate	73.0
Potassium chlorate	3.3

The solubility of a solute in a given solvent varies appreciably with temperature and to a small extent with the size of the particles. Generally speaking, the higher the temperature, the greater is the solubility and the finer the particles the greater is the solubility.

Variation of solubility with temperature. The solubilities of some common inorganic compounds in water at different temperatures are plotted in Fig. 6.1. Such curves are known as **solubility curves**. It is evident that solubilities of most of the substances increase with rise in temperature, the increase in some cases (e.g., KNO_3 , NH_4Br) being much more than in others [e.g., NH_4Cl , $\text{Al}_2(\text{SO}_4)_3$], while in some cases (e.g., NaCl) the increase is very slight indeed. The solubilities of very few substances decrease with rise in temperature. The examples are furnished by calcium sulphate, calcium hydroxide, sodium sulphate (anhydrous) and cerium sulphate.

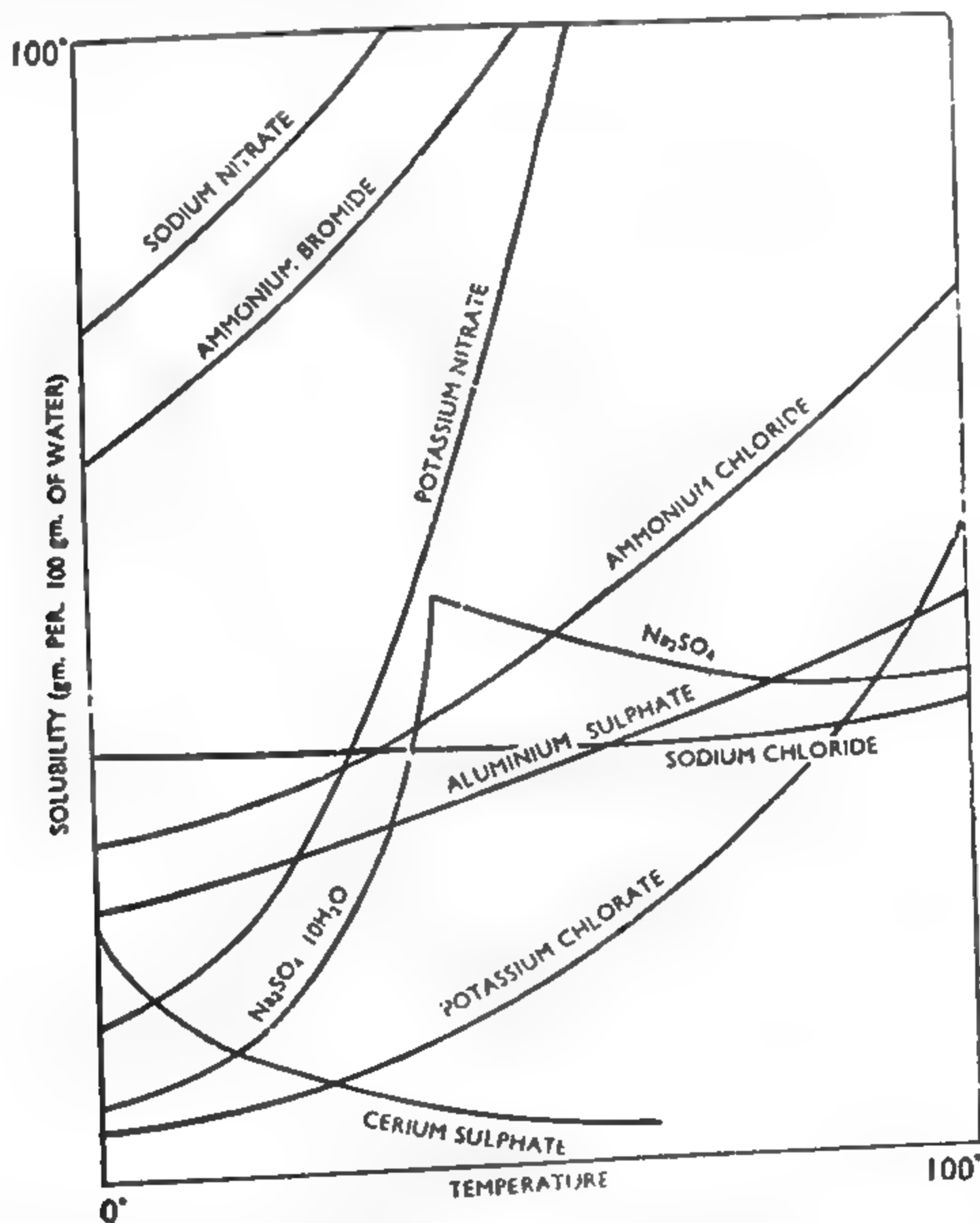


Fig. 6.1. Solubility curves of different solutes.

The solubility curve of sodium sulphate has one other peculiarity. The solubility first increases with rise in temperature up to 32.3° and

decreases thereafter. Actually, the first part of the curve represents the solubility of sodium sulphate decahydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, the solubility of which increases with temperature. The latter part represents the solubility curve of sodium sulphate anhydrous, Na_2SO_4 , the solubility of which decreases with rise in temperature. The temperature at which the two parts of the curve meet, *i.e.*, 32.3° , gives the transition temperature between the decahydrate and the anhydrous sodium sulphate, *i.e.*,



In accordance with Le Chatelier principle, those substances which absorb heat (*i.e.*, produce cooling) on dissolution are more soluble at higher temperatures while those substances which evolve heat on dissolution are less soluble at higher temperatures.

Fractional Crystallisation.

The fact that different substances are soluble in water (or any other solvent) to different extents and that the variation of temperature influences their respective solubilities in various ways, is made use of in separating different solutes from one another. The mixture of two or more solutes is dissolved in a suitable solvent at a suitable temperature. On gradual cooling, the solution becomes saturated with respect to the least soluble solute first and this begins to separate out. On further continued cooling, the other solutes also separate out *in the order of their decreasing solubility*. This process is known as **fractional crystallization** and is widely used for the preparation and purification of many substances. Actually, the operation has to be repeated a number of times and involves a number of stages.

QUESTIONS

1. Explain the terms solution, saturated solution and super-saturated solution. Give examples.
2. What is meant by the term solubility? How would you proceed to determine the solubility of a salt in water at the room temperature?
3. Explain the term solubility. How does the solubility vary with temperature?
4. Explain the principle of fractional crystallisation for the separation of two solutes from a solution.

CHAPTER VII

OXIDATION AND REDUCTION

Oxidation, in a narrow sense, is defined as a reaction in which a substance combines with oxygen. The substance combining with oxygen is said to be *oxidised* while the substance that supplies the oxygen is known as an *oxidising agent*. For example, when carbon burns in air to form carbon dioxide,



carbon is said to be oxidised and oxygen of the air is said to be the oxidising agent.

Similarly, **reduction**, in a narrow sense, is defined as a reaction in which oxygen is removed from a compound. The compound is said to be *reduced* and the substance removing the oxygen is termed as the *reducing agent*. Thus, in the reaction,



ferric oxide is said to be reduced and hydrogen acts as the reducing agent.

Oxidation, in a broader sense, is defined as a reaction which involves (i) *Addition of oxygen* or (ii) *that of any non-metal element (other than hydrogen)* or (iii) *removal of hydrogen* or (iv) *that of any metal* or (v) *increase of valency of a metal*.

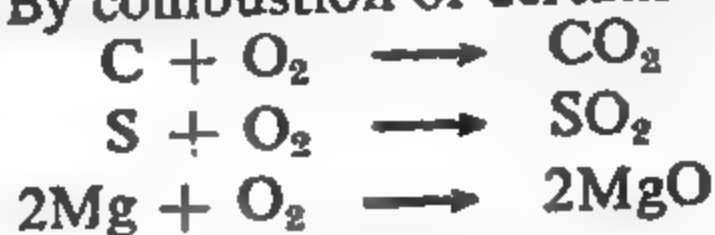
A substance which can bring about an oxidation reaction is known as an oxidising agent.

Reduction, in a broader sense, is just the reverse of the above processes. Thus, reduction involves (i) *removal of oxygen* or (ii) *that of any non-metal element (other than hydrogen)* or (iii) *addition of hydrogen* or (iv) *that of any metal* or (v) *decrease of valency of a metal*.

A substance which can bring about reduction is known as a reducing agent.

Examples of Oxidation. A few examples of oxidation reactions brought about by using different oxidising agents are given below :

(i) **With oxygen.** By combustion of certain elements in air :

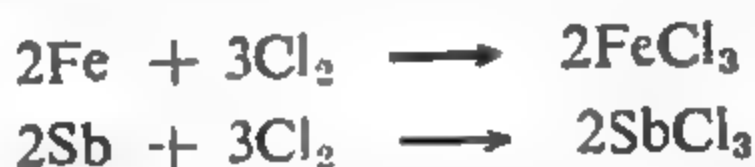


or by absorption of atmospheric oxygen :



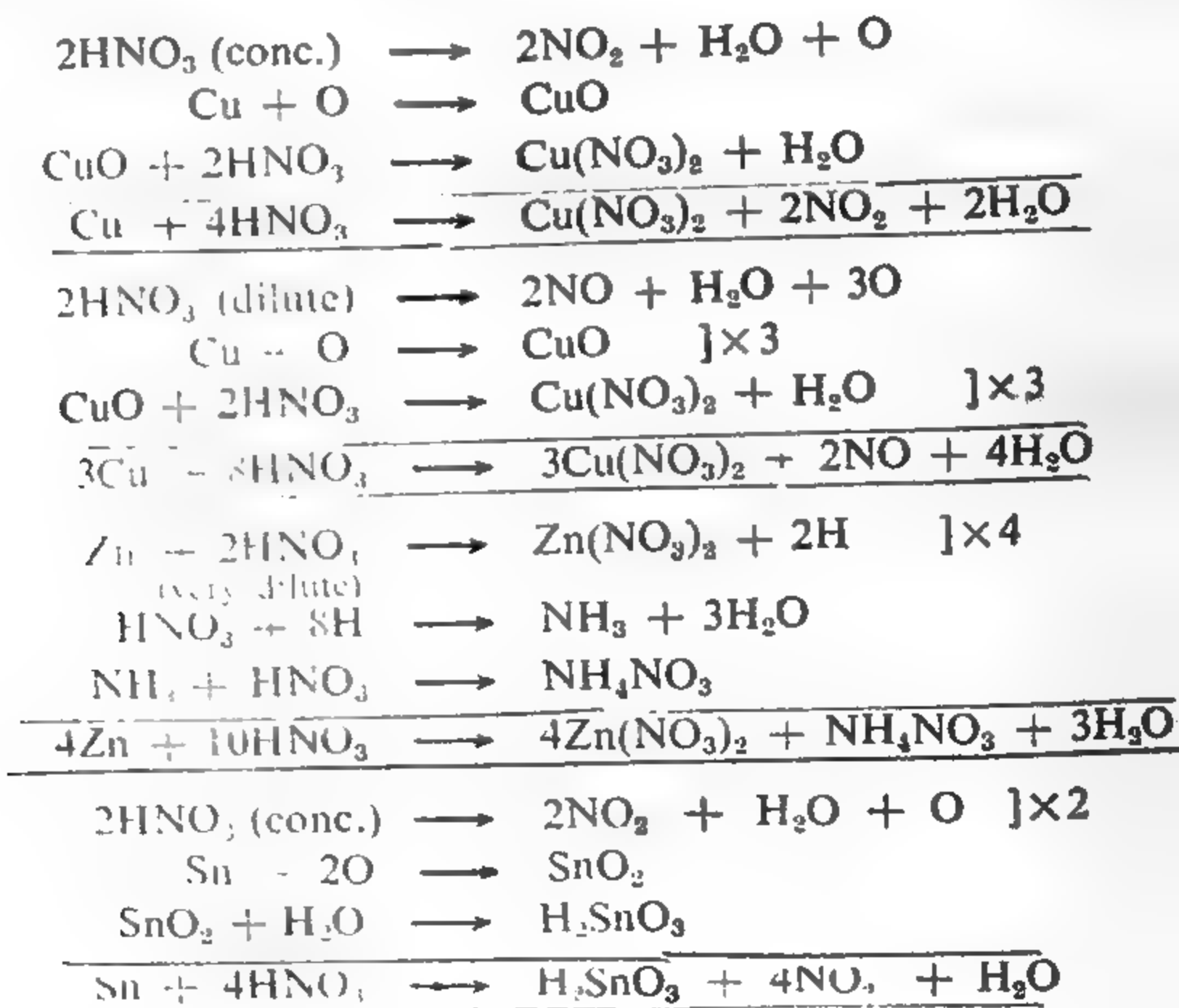
In all the above reactions **oxygen is added**. Thus, carbon, sulphur, magnesium and nitrous acid are said to be oxidised to carbon dioxide, sulphur dioxide, magnesium oxide, and nitric acid, respectively.

(ii) **With chlorine.** Chlorine combines with a number of metals when they are hot.



In these reactions a **non-metal element (chlorine) is added**. Thus, iron and antimony are said to be oxidised to ferric chloride and antimony chloride respectively.

(iii) **With nitric acid** Nitric acid oxidises many metals to nitrates and itself gets reduced to lower oxides of nitrogen or ammonium nitrate depending upon the nature of the metal and the concentration of the acid.



(iv) **With a dioxide.** Manganese dioxide is a good oxidising agent :



Hydrochloric acid is said to be oxidised to chlorine. This is a case of **removal of hydrogen**.

(v) **With a peroxide.** Hydrogen peroxide is a good oxidising agent. Thus, it oxidises potassium iodide to iodine.



This is a case of **removal of a metal**.

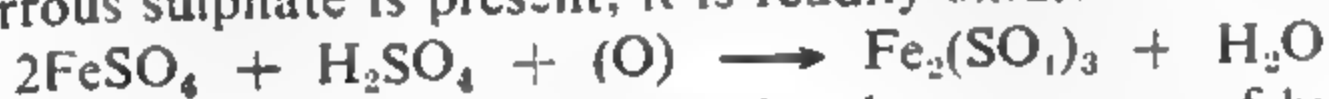
Hydrogen peroxide also oxidises lead sulphide to lead sulphate.



(iv) **With acidified solutions of potassium permanganate and potassium dichromate.** Potassium permanganate and potassium dichromate in acid solutions act as strong oxidising agents. In the presence of sulphuric acid the reactions are represented as :



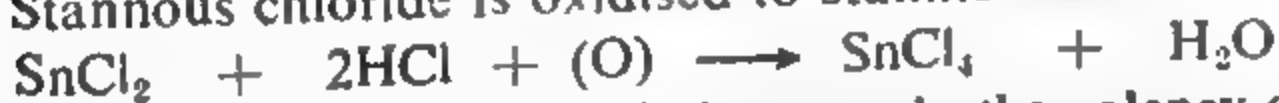
If a reducing agent capable of taking up oxygen is present, the above reactions proceed more and more towards the right. Thus, if ferrous sulphate is present, it is readily oxidised to ferric sulphate.



Similarly, ferrous chloride in the presence of hydrochloric acid is oxidised to ferric chloride.



Stannous chloride is oxidised to stannic chloride.

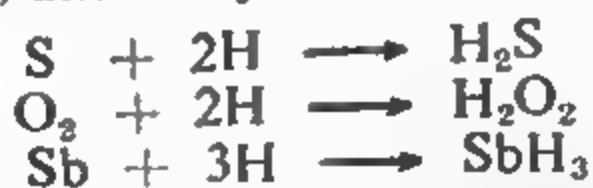


In these reactions, there is **increase in the valency of metals** (iron and tin).

Examples of Reduction. A few examples of reduction brought about by using different reducing agents are given below :

(i) **With hydrogen.** Hydrogen gas is a poor reducing agent because its molecule is highly stable and a considerable amount of energy is required to break it into atoms. Atomic hydrogen is, however, highly reactive. It can be prepared by passing an electric discharge of a high potential through hydrogen gas at reduced pressure.

Atomic hydrogen reduces sulphur to hydrogen sulphide, oxygen to hydrogen peroxide, antimony to its hydride,



and so on. Each reaction involves **addition of hydrogen**.

(ii) **With metals.** Certain metals, like aluminium, are good reducing agents. This is on account of the readiness with which they can take up oxygen at high temperatures. Aluminium, for instance, takes up

oxygen readily from ferric oxide on heating.



A considerable amount of heat is evolved in the reaction which is used in the thermite welding of steel. Zinc reduces phenol to benzene.



Each of the above reactions involves removal of oxygen.

(iii) **With carbon.** Amongst the non-metals, carbon is a useful reducing agent and is used in metallurgical processes. For example, zinc oxide is reduced by coke when heated in closed retorts.



This reaction also involves removal of oxygen.

(iv) **With ammonia.** Ammonia, on account of its hydrogen, acts as a reducing agent in certain reactions.



The first reaction involves removal of oxygen from copper oxide while the second involves the addition of hydrogen to chlorine.

(v) **With hydrogen sulphide.** Hydrogen sulphide also, on account of its hydrogen, acts as a reducing agent. For example, it reduces ferric salts to ferrous state.



This reaction involves removal of a non-metal element (chlorine from ferric chloride). The reaction also involves decrease in the valency of a metal (iron).

(vi) **With sulphur dioxide.** Sulphur dioxide has a tendency to take up oxygen to form sulphur trioxide. Therefore, it tends to remove oxygen wherever possible.



Sulphur dioxide can also reduce ferric salts to ferrous state and stannic salts to stannous state.



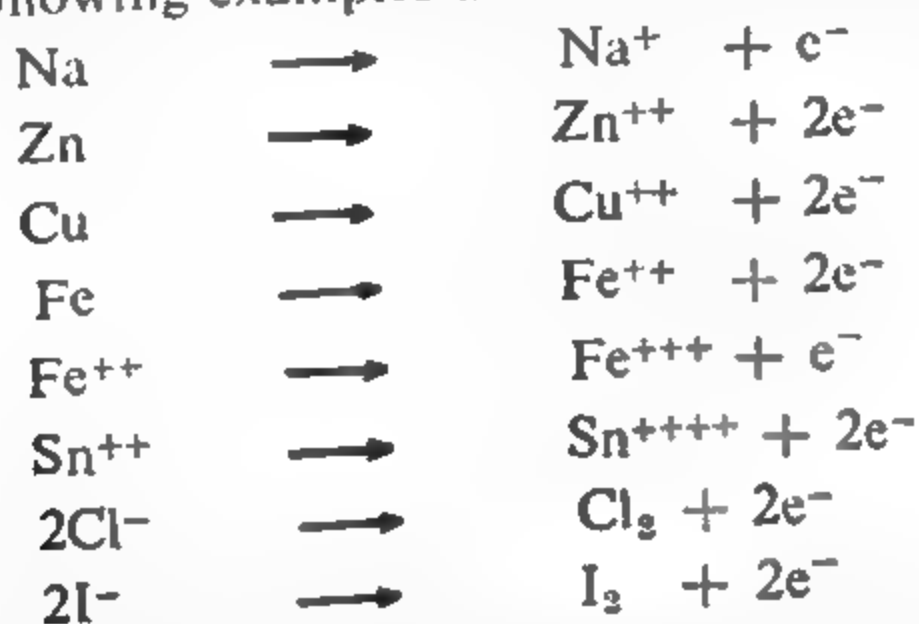
Concurrence of Oxidation and Reduction. In all the reactions considered above, it will be seen that oxidation and reduction proceed concurrently, i.e., side by side. For example, in the reaction of lead sulphide and hydrogen peroxide, while the former is oxidised to lead sulphate, the latter is reduced to water. Similarly, in the reaction between ferric oxide and aluminium, while the former is reduced to iron, the latter is oxidised to aluminium oxide.

Modern Concepts.

Oxidation and reduction are now used in much wider and more general sense. Two different methods of interpreting such reactions have been developed. One of these is based on electronic interpretation and is useful when the reactants are in the ionic states. The other is based on the arbitrary concept of oxidation numbers and is universally applicable to ionic as well as non-ionic reactants. But this is beyond the scope of the present volume.

The Electronic Interpretation of Oxidation – Reduction Processes.

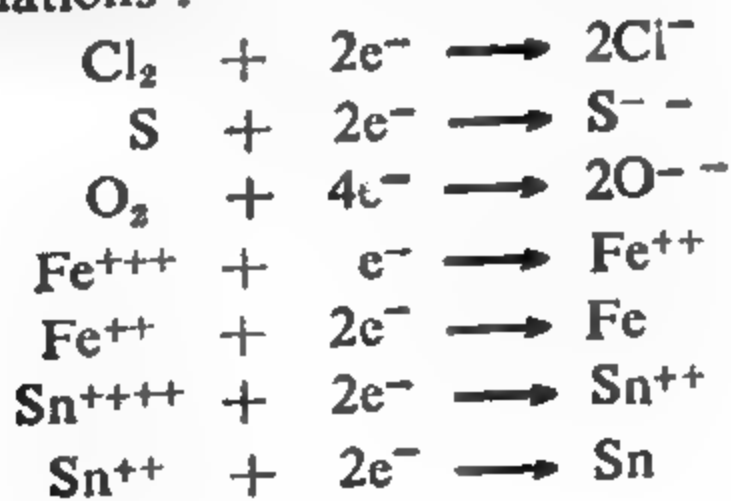
According to electronic interpretation, **oxidation** is defined in a general sense, as a reaction in which an atomic system changes into a more electropositive or less electronegative state by loss of one or more electrons. The following examples are illustrative of oxidation :



In the first four examples, neutral atoms lose one or more electrons to change into positive ions (higher electropositive condition). In the fifth case the positive ferrous ion, carrying two positive charges loses one more electron and changes into a higher electropositive condition producing ferric ion carrying three positive charges. In the last two examples, negative ions lose electrons and change into neutral molecules (higher electropositive condition). Thus, in each case an atomic system has changed into more electropositive (or less electronegative) state by the loss of electrons.

The equations like the above, in which electrons are produced, are known as **oxidation half-reactions**.

Reduction, according to the electronic concept, is defined broadly as a reaction in which an atomic system changes into less electropositive (or more electronegative) state, by the gain of electrons. Consider the following equations :



In the first three examples, neutral atoms or molecules take up electrons to change into negative ions while in the last examples, positive ions gain electrons to change into either less positively charged ions or neutral atoms.

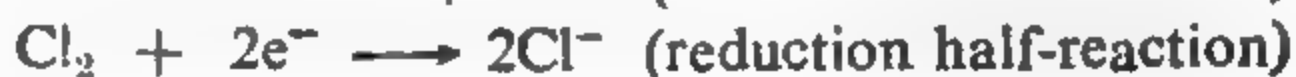
Such equations as the above, in which electrons are accepted, are known as **reduction half reactions**.

Oxidation-Reduction. oxidation is always accompanied by an equivalent amount of reduction. This is because the electrons, lost in an oxidation system, must be accepted by a system undergoing reduction. Therefore, an oxidation-reduction reaction can take place by combination of an oxidation half-reaction with a reduction half-reaction.

Consider, for example, the reaction between sodium (solid) and chlorine (gas) resulting in the formation of sodium chloride (solid). The complete reaction is represented by the equation :



The half reactions are :



Adding the two :



The number of electrons lost by sodium is equal to the number of electrons gained by chlorine. Sodium chloride actually consists of Na^+ and Cl^- ions in the crystal.

In the above reaction, sodium is said to be oxidised to Na^+ . This has been brought about by the taking up of the electrons by chlorine. Therefore, *chlorine acts as an oxidising agent*.

An oxidising agent is a substance which can take up electrons.

It is also evident that chlorine, in the above reaction, is reduced to chloride ion (Cl^-). This has been possible by the furnishing of electrons by sodium. Thus, *sodium is a reducing agent*.

A reducing agent is a substance which furnishes electrons.

To sum up :

Oxidation is a process (reaction) in which one or more electrons are furnished.

Reduction is a process (reaction) in which electrons are accepted.

Oxidising agent is a substance which can accept electrons.

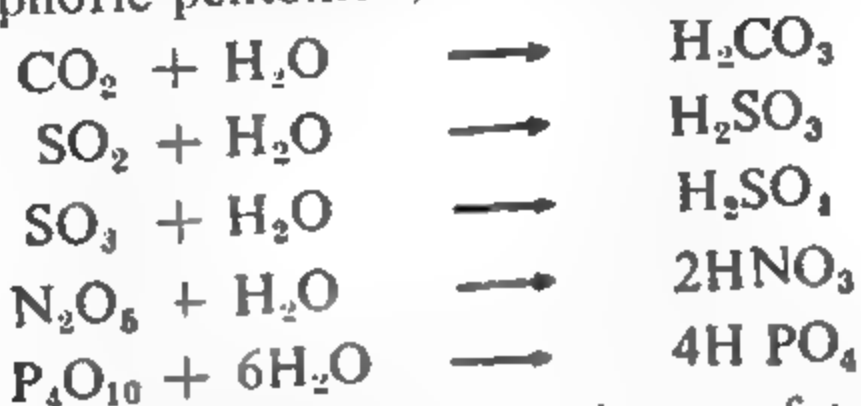
Reducing agent is a substance which can furnish electrons.

In the various equations given above Na , Zn , Cu , Fe , Fe^{++} , Sn^{++} , Cl^- , S^{--} are reducing agents while Cl_2 , S , O_2 , Fe^{+++} , Sn^{++++} , etc., are oxidising agents.

CLASSIFICATION OF OXIDES

The oxides can be conveniently divided into the following six types :

1. Acidic Oxides. The oxides of non-metals, in particular, give acidic reactions and are called acidic oxides. They dissolve in water forming acids and are, therefore, called *acid anhydrides*. The examples are carbon dioxide, sulphur dioxide, sulphur trioxide, nitrogen pentoxide, phosphoric pentoxide, etc.



Some of the acidic oxides give a mixture of two acids when allowed to react with water. Thus, nitrogen dioxide gives a mixture of nitrous and nitric acids and is called a *mixed anhydride*.



They form mixtures of two salts when allowed to react with alkalies, e.g.,



2. Basic Oxides. The oxides of most of the metals, in particular, give basic reactions and are called basic oxides. If they are soluble in water they give alkaline solutions and are themselves known also as alkalies. For example,



Basic oxides react with acids forming salt and water, e.g.,



3. Neutral Oxides. These oxides do not show any tendency to form salts when treated with acids or bases. The examples are carbon monoxide and nitrous oxide.

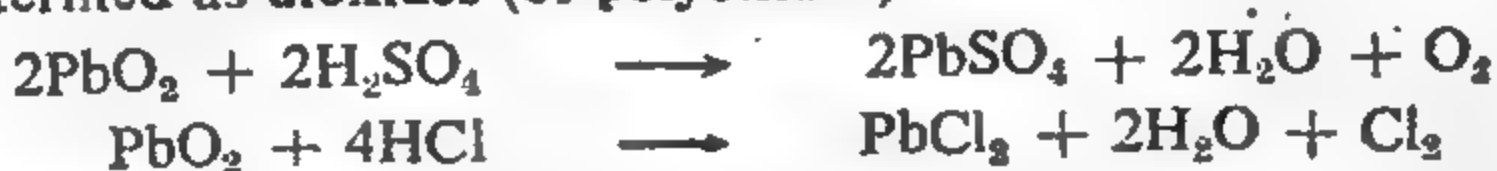
4. Amphoteric Oxides. There are a number of oxides which behave as acids and also as bases, depending upon the conditions. Thus, zinc oxide behaves as an acidic oxide when treated with concentrated sodium hydroxide and as a basic oxide when treated with hydrochloric acid.



5. Peroxides. True peroxides are those oxides which form hydrogen peroxide when treated with dilute acids. For example,



There are certain higher oxides which on treatment with sulphuric acid yield oxygen and on treatment with hydrochloric acid yield chlorine. These are termed as **dioxides** (or **polyoxides**).



6. **Compound Oxides.** Some of the oxides behave as if they are compounds of two oxides. For example, ferroso-ferric oxide, Fe_3O_4 , behaves as a compound of FeO (ferrous oxide) and Fe_2O_3 (ferric oxide), as on treatment with an acid it gives a mixture of ferrous and ferric salts.



Similarly, red lead, Pb_3O_4 , behaves as a compound of 2PbO and PbO_2 . On treatment with nitric acid it forms lead nitrate and lead dioxide is deposited.



Equivalent Weights of Oxidising Agents. *The equivalent weight of an oxidising agent is that weight of it which takes up one electron.* In other words, the equivalent weight of an oxidising ion (or compound) is given by the ion weight (the molecular weight) of the substance divided by the number of electrons gained by it per ion (or molecule).

Thus, the equivalent weight of ferric ion which can gain one electron to change to ferrous ion



is the same as its ion weight, viz., 56 gms. Accordingly, the equivalent weight of ferric chloride is the same as its molecular weight.

Stannic ion can gain two electrons in its reduction.



Hence, the equivalent weight is *half the weight of the ion*.

Accordingly, the equivalent weight of stannic chloride is equal to half of its molecular weight.

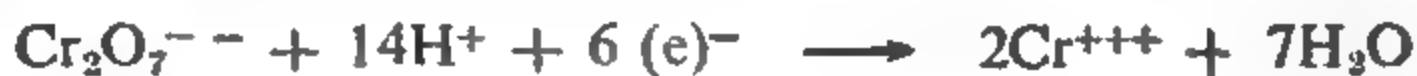
The permanganate ion in acid solution can gain five electrons in its reaction as discussed below :



Therefore, the equivalent weight is *one fifth of the weight of the ion*, that is, $119 \div 5 = 23.8$ gms.

Accordingly, the equivalent weight of any permanganate is equal to one fifth of its molecular weight. Thus, the equivalent weight of potassium permanganate is 31.6 gms.

The oxidation reactions of dichromate ion in acid solution proceed with the gain of six electrons.



Hence, the equivalent weight of the dichromate ion is *one sixth of the gram ion weight*, $216 \div 6 = 36.0$ gms.

The equivalent weight of potassium dichromate is $294 \div 6 = 49.0$ gms.

Equivalent Weight of Reducing Agents. On similar considerations as above, the equivalent weight of a reducing ion or compound is defined as *that weight of it which loses one electron*. In other words, the equivalent weight of a reducing ion (or compound) is given by the ion weight (or molecular weight) divided by the number of electrons lost per ion (or molecule). Thus, the equivalent weight of ferrous ion (Fe^{++}) is the same as the ion weight because it loses only one electron to change into ferric ion (Fe^{+++}) while that of stannous ion (Sn^{++}) is equal to the ion weight divided by 2 because it loses two electrons to change into stannic ion (Sn^{++++}).

The sulphide ion loses two electrons to be oxidised to sulphur,



and, therefore, its equivalent weight is *half the ion weight* and the equivalent weight of any sulphide such as Na_2S or CaS is half the molecular weight of the compound.

The equivalent weight of an oxalate ion is half the weight of the ion because its oxidation takes place as



Accordingly, the equivalent weight of oxalic acid or any of its salts is given by half the molecular weight of the compound.

The equivalent weight of a sulphite as well as that of a thiosulphate is also equal to half the molecular weight because their oxidations proceed as :



QUESTIONS

1. Define Oxidation and Reduction as understood at the present time. Give at least four examples of each.

2. What are oxidising and reducing agents? Name four oxidising and four reducing agents. Give one reaction of each.

Give oxidation reactions brought about by the following oxidising agents:

(1) Chlorine (2) Hydrogen peroxide (3) Nitric acid (4) Acidified [potassium permanganate].

4. Give reducing reactions brought about by the following reducing agents:

(1) Hydrogen (2) Aluminium (3) Carbon (4) Hydrogen Sulphide and (5) Sulphur dioxide.

5. Explain how oxidation, reduction reactions in aqueous solutions have been interpreted on the basis of transference of ions. Give examples.

6. What do you understand by equivalent weights of oxidising and reducing agents? Give examples.

7. How will you determine the equivalent weights of the following :

(1) Potassium permanganate (2) Potassium dichromate (3) Ferric chloride.

8. Define equivalent weight of a reducing agent. How will you determine the equivalent weights of the following reducing agents :

(1) Oxalic acid (2) Sodium sulphide (3) Sodium sulphite (4) Sodium thiosulphate.

9. What tests would you apply to a given substance to show whether it is an oxidising or a reducing agent? Classify the following substances into oxidising and reducing agents, giving examples of their behaviour :

HNO_3 , H_2S , SnCl_2 and Cl_2

10. Explain the significance of the terms : Oxidation and Reduction. Name three oxidising and three reducing agents as used in inorganic chemistry. With the help of equations and an example in each case, explain the action of each.

11. Explain with illustrative examples the terms oxidation and reduction. How many types of oxides are there? What types of oxides are the following :

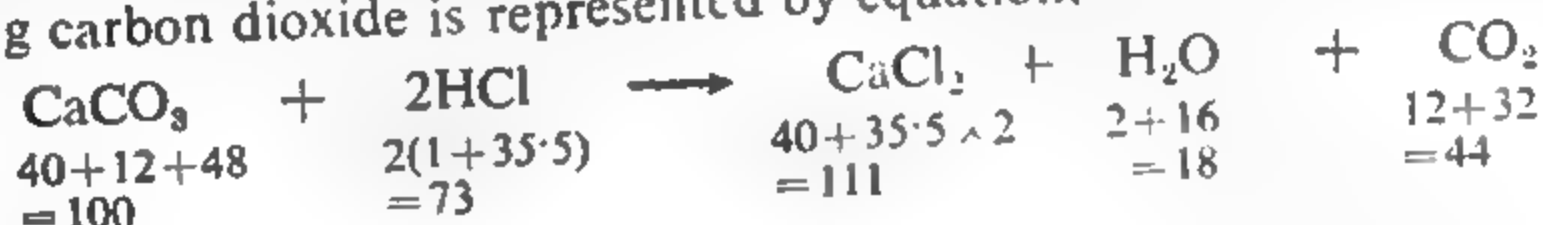
Barium peroxide, Water, Lead tetroxide, Carbon dioxide.

(Jammu & Kashmir T.D.C. (I) 1967)

CHAPTER VIII

PROBLEMS BASED ON CHEMICAL EQUATIONS

A chemical equation, as is well-known, represents not only the formulae but also the relative weights of the reactants and products of a chemical reaction. For example, the well-known reaction between calcium carbonate and hydrochloric acid forming calcium chloride, water and liberating carbon dioxide is represented by equation,



Evidently,

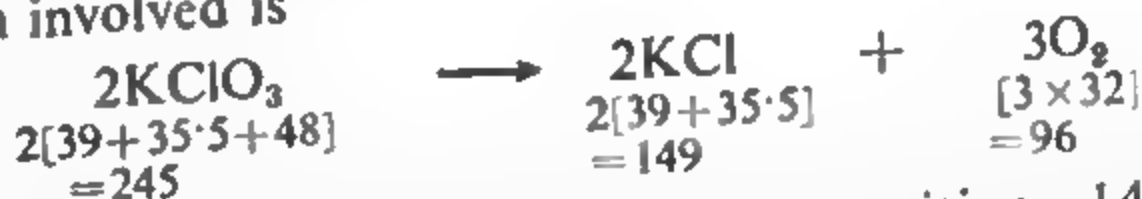
100 gm. of calcium carbonate require 73 gm. of hydrochloric acid to produce 111 gm. of calcium chloride, 18 gm. of water and 44 gm. (or 22.4 litres at N.T.P.) of carbon dioxide.

A chemical equation, therefore, permits calculations of the amounts (weights or volumes) of products obtained from a given amount of the reactants, and vice versa.

(1) Problems based on Weight-relations in Chemical Equations.

Example 1. Calculate the weights of potassium chloride and oxygen obtained by complete decomposition of 5.5 gm. of potassium chlorate. [$K=39$, $Cl=35.5$, $O=16$].

The reaction involved is



245 gm. of potassium chlorate yield on decomposition = 149 gm. of potassium chloride

\therefore 5.5 gm. of potassium chlorate will yield

$$= \frac{149}{245} \times 5.5 \text{ gm.}$$

$$= 3.345 \text{ gm. of potassium chloride}$$

(b) 245 gm. of potassium chlorate yield = 96 gm. of oxygen

∴ Weight of oxygen obtained by complete decomposition of 5.5 gm.

$$\begin{aligned} \text{of potassium chlorate} &= \frac{96}{245} \times 5.5 \\ &= 2.155 \text{ gm.} \end{aligned}$$

Example 2. If hydrochloric acid contains 20 per cent by weight of HCl, the remaining being water, what weight of this acid will be required for reacting completely with 50 gm. of calcium carbonate?

The reaction involved is



100 gm. of CaCO_3 require for complete reaction

$$= 73 \text{ gm. of HCl (100\% pure)}$$

$$\begin{aligned} \therefore 50 \text{ gm. of } \text{CaCO}_3 \text{ will require} &= \frac{73}{100} \times 50 \text{ gm. of HCl} \\ &= 36.5 \text{ gm.} \end{aligned}$$

Since the given acid is only 20% pure, therefore, the weight of this acid

$$\begin{aligned} \text{required} &= \frac{100}{20} \times 36.5 \\ &= 182.5 \text{ gm.} \end{aligned}$$

Example 3. 5.0 gm. of iceland spar (CaCO_3) was added to 7.5 gm. of dilute hydrochloric acid. After the reaction was over, it was found that 0.50 gm. of iceland spar was left undissolved. Calculate the percentage strength of hydrochloric acid.

The reaction involved is



Wt. of iceland spar (CaCO_3) taken = 5.0 gm.

Wt. of hydrochloric acid taken = 7.5 gm.

Wt. of CaCO_3 left unused = 0.50 gm.

∴ Wt. of CaCO_3 reacted = $5.0 - 0.5 = 4.5 \text{ gm.}$

According to the above equation,

$$100 \text{ gm. of } \text{CaCO}_3 \equiv 73 \text{ gm. of HCl}$$

$$\therefore 4.5 \text{ gm. } \text{CaCO}_3 = \frac{73}{100} \times 4.5 = 3.285 \text{ gm. of HCl}$$

In other words, 7.50 gm. of dilute hydrochloric acid contained only 3.285 gm. of HCl

Hence, percentage strength of hydrochloric acid

$$= \frac{3.285}{7.50} \times 100 = 43.80 \text{ gm.}$$

Example 4. One gram of a silver ore was dissolved in nitric acid and silver chloride weighed 0.7880 gm. Calculate the percentage of silver in the ore. ($\text{Ag}=108$; $\text{Cl}=35.46$).

The reaction involved is



According to the above equation,

$$143.46 \text{ gm. AgCl} \equiv 170 \text{ gm. of AgNO}_3$$

$$\begin{aligned} \therefore 0.7880 \text{ gm. of AgCl} &\equiv \frac{170}{143.46} \times 0.7880 \text{ gm. of AgNO}_3 \\ &= 0.9338 \text{ gm.} \end{aligned}$$

In other words, 0.9338 gm. of silver nitrate was present in the nitric acid solution of the ore.

Since 1 gm. molecule of $\text{AgNO}_3 \equiv 1$ gm. atom of Ag

i.e., $170 \text{ gm. AgNO}_3 \equiv 108 \text{ gm. of Ag}$

\therefore Wt. of Ag corresponding to 0.9338 gm. of silver nitrate

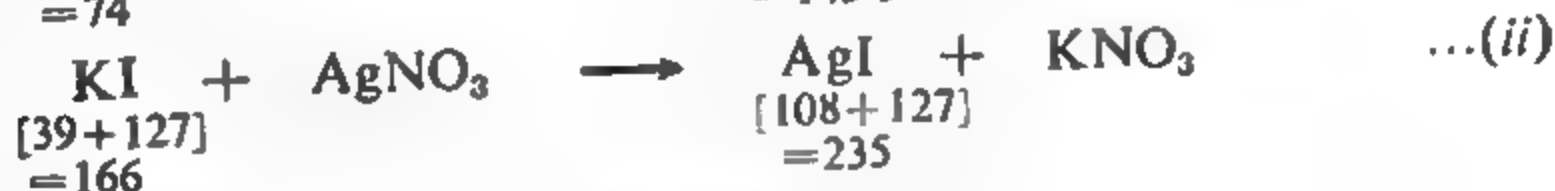
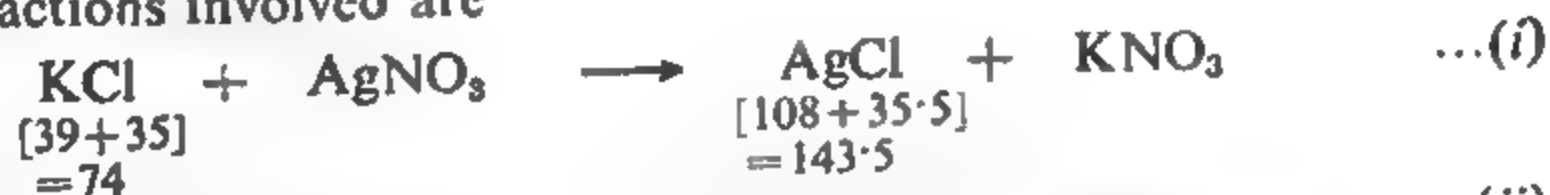
$$\begin{aligned} &= \frac{108}{170} \times 0.9338 \text{ gm.} \\ &= 0.5932 \text{ gm.} \end{aligned}$$

And this weight of Ag (i.e., 0.5932 gm.) is present in 1 gm. of the ore. Therefore, the percentage of Ag in the ore $= 0.5932 \times 100$
 $= 59.32$

Example 5. 0.5 gm. of a mixture of KCl and KI dissolved in water and precipitated with silver nitrate gave 0.809 gm. of silver chloride and silver iodide. Calculate the percentage of KI in the mixture.

($\text{K}=39$, $\text{Cl}=35.5$, $\text{I}=127$, $\text{Ag}=108$).

The reactions involved are



Let the weight of KCl in the mixture be $= x$ gm.

\therefore The weight of KI in the mixture $= (0.5-x)$ gm.

Now, according to equation (i),

74.5 gm. of KCl yield 143.5 gm. of AgCl

$\therefore x$ gm. of KCl will yield $\frac{143.5}{74.5} \times x$ gm. of AgCl ...(iii)

and according to equation (ii),

166 gm. of KI yield 235 gm. of AgI

$$\therefore (0.5-x) \text{ gm. of KI will yield } \frac{235}{166} \times (0.5-x) \text{ gm. of AgI} \quad \dots(iv)$$

Hence, the total wt. of AgCl and AgI obtained must be equal to the sum of (iii) and (iv) $= \frac{143.5}{74.5} x + \frac{235}{166} \times (0.5-x) \text{ gm.}$

But actually the wt. of AgCl and AgI obtained = 0.809 gm.

$$\therefore \frac{143.5}{74.5} x + \frac{235}{166} \times (0.5-x) = 0.809$$

or

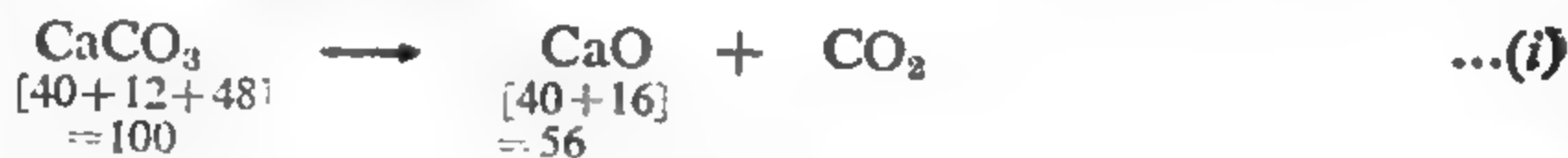
$$x = 0.2$$

$$\therefore \text{Wt. of KI in the mixture} = (0.5-x) = (0.5-0.2) = 0.3$$

$$\begin{aligned} \therefore \text{Percentage of KI} &= \frac{0.3}{0.5} \times 100 \\ &= 60.0 \end{aligned}$$

Example 6. 1.84 gm. of a mixture of CaCO_3 and MgCO_3 is strongly heated till no further loss in weight takes place. The residue weighs 0.96 gm. Find the percentage composition of the mixture.

The reactions involved are



Let the wt. of CaCO_3 in the mixture = x gm.

$$\therefore \text{Wt. of } \text{MgCO}_3 \text{ in mixture} = (1.84-x) \text{ gm.}$$

According to equation (i),

$$100 \text{ gm. of } \text{CaCO}_3 \text{ leave a residue} = 56 \text{ gm.}$$

$$\therefore x \text{ gm. of } \text{CaCO}_3 \text{ will leave a residue} = \frac{56}{100} \times x \text{ gm.}$$

and according to equation (ii)

$$84 \text{ gm. of } \text{MgCO}_3 \text{ leave a residue} = 40 \text{ gm.}$$

$$\begin{aligned} \therefore (1.84-x) \text{ gm. of } \text{MgCO}_3 \text{ will leave a residue} \\ = \frac{40}{84} (1.84-x) \text{ gm.} \end{aligned}$$

Therefore, the total wt. of residue left

$$= \frac{56}{100} \times x + \frac{40}{84} (1.84-x) \text{ gm.}$$

But actually the weight of the residue left = 0.96 gm.

$$\frac{56}{100}x + \frac{40}{84}(1.84 - x) = 0.96$$

$$\therefore x = 1.0$$

or Wt. of CaCO_3 in the mixture = 1.0 gm.

$$\therefore \% \text{ age of } \text{CaCO}_3 = \frac{1.0}{1.84} \times 100 = 54.35$$

$$\text{and } \% \text{ age of } \text{MgCO}_3 = 100 - 54.35 = 45.65$$

II. Problems based on Weight-Volume relations in Chemical Equations.

Example 7. What weight of sulphuric acid will be required to completely dissolve 3 gm. of magnesium carbonate? Calculate the volume of carbon dioxide evolved at N.T.P.

The reaction involved is



According to this equation,

$$84 \text{ gm. of } \text{MgCO}_3 \text{ require} = 98 \text{ gm. of } \text{H}_2\text{SO}_4$$

$$\therefore 3 \text{ gm. of } \text{MgCO}_3 \text{ will require} = \frac{98}{84} \times 3 \text{ gm.} = 3.5 \text{ gm. of } \text{H}_2\text{SO}_4$$

Further,

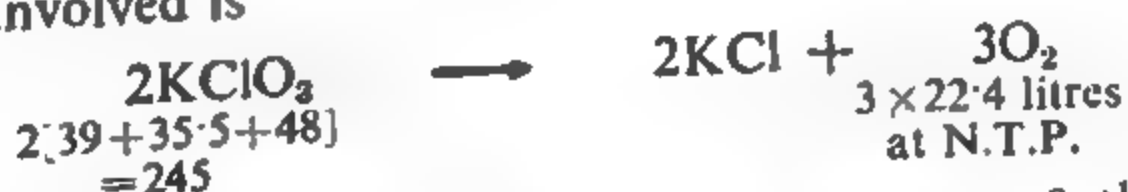
According to the above equation.

84 gm. of MgCO_3 on complete reaction with acid, evolve 22.4 litres of carbon dioxide at N.T.P.

$$\begin{aligned} \therefore 3 \text{ gm. of } \text{MgCO}_3 \text{ will evolve} &= \frac{22.4}{84} \times 3 \\ &= 0.8 \text{ litres} \\ &= 800 \text{ c.c. of } \text{CO}_2 \text{ at N.T.P.} \end{aligned}$$

Example 8. What volume of oxygen at 17°C and 760 mm. pressure would be obtained by heating 100 gm. of KClO_3 of 85% purity?

The reaction involved is



It is given that KClO_3 is 85% pure, therefore, 100 gm. of the impure sample will contain 85 gm. of KClO_3 .

According to the above equation,

245 gm. of KClO_3 evolve = 3×22.4 litres of oxygen at N.T.P.

$$\therefore 85 \text{ gm. of } \text{KClO}_3 \text{ evolve} = \frac{3 \times 22.4}{245} \times 85 \text{ litres of oxygen at N.T.P.}$$

$$= 23.31 \text{ litres at N.T.P.}$$

As the experiment is performed at 17°C and 760 mm. pressure, the above volume must be reduced to 17°C and 760 mm. pressure by the application of the gas equation :

$$\frac{P_1 V_1}{T_1} = \frac{P_N V_N}{T_N}$$

where	$V_N = 23.31 \text{ litres}$	$V_1 = ?$
	$P_N = 760 \text{ m.m.}$	$P_1 = 760 \text{ mm.}$
	$T_N = 273^\circ\text{A}$	$T_1 = 273 + 17 = 290^\circ\text{A}$

Substituting these values in the gas equation, we have

$$\frac{V_1 \times 760}{290} = \frac{23.31 \times 760}{273}$$

or $V_1 = 24.76 \text{ litres}$

Example 9. 0.5 gm. of impure zinc on treatment with dilute hydrochloric acid gave 160 c.c. of moist hydrogen at 16°C and 755 mm. pressure. Calculate the percentage of zinc in the above sample. ($\text{Zn} = 65.4$; Aq. tension at $16^\circ\text{C} = 13.53 \text{ mm.}$)

The reaction involved is



According to the above equation,

65.4 gm. of zinc evolve 22.4 litres of hydrogen at N.T.P.

Now the volume of moist hydrogen evolved at 16°C and 755 mm. pressure is 160 c.c.

Volume of dry hydrogen at N.T.P. is calculated by making use of gas equation

$$\frac{P_1 V_1}{T_1} = \frac{P_N V_N}{T_N}$$

$V_1 = 160 \text{ c.c.}$	$V_N = ?$
$P_1 = 755 - 13.53$ 741.47 mm.	$P_N = 760 \text{ mm.}$
$T_1 = 273 + 16 = 289^\circ\text{A}$	$T_N = 273^\circ\text{A}$

or
$$\frac{160 \times 741.37}{289} = \frac{760 \times V_N}{273}$$

$$V_N = \frac{160 \times 741.47 \times 273}{289 \times 760}$$

$$= 147.4 \text{ c.c.}$$

Now 22.4 litres of hydrogen are evolved from 65.4 gm. of zinc

$$\therefore 147.4 \text{ c.c. of hydrogen will be evolved from } = \frac{65.4}{22,400} \times 147.4$$

$$= 0.4304 \text{ gm. of Zn}$$

$$\text{Wt. of impure zinc taken} = 0.5 \text{ gm.}$$

$$\therefore \text{Percentage of pure zinc in the sample} = \frac{0.4304}{0.5000} \times 100$$

$$= 86.08$$

Example 10. A naturally occurring mineral was found to contain (i) 42% MgCO_3 (ii) 55% CaCO_3 and the rest was impurity. What volume of CO_2 measured at 15°C and 745 mm. pressure will be evolved by heating 10 gm. of the mineral with hydrochloric acid.

The reactions involved are



$$\begin{array}{ll} \text{Since the weight of the mineral taken} & = 10 \text{ gm.} \\ \therefore \text{Wt. of MgCO}_3 \text{ in 10 gm. of the mineral} & = 4.2 \text{ gm.} \\ \text{Wt. of CaCO}_3 \text{ in 10 gm. of the mineral} & = 5.5 \text{ gm.} \end{array}$$

The impurity is not affected by the acid.

According to equation (i),

84 gm. of MgCO_3 liberate 22.4 litres of CO_2 at N.T.P.

$$\therefore 4.2 \text{ gm. of MgCO}_3 \text{ will liberate } \frac{22.4}{84} \times 4.2 \text{ litres of CO}_2 \text{ at N.T.P.}$$

$$= 1.12 \text{ litres of CO}_2 \text{ at N.T.P.}$$

Again, according to equation (ii),

100 gm. of CaCO_3 liberate 22.4 litres of CO_2 at N.T.P.

$$\therefore 5.5 \text{ gm. of CaCO}_3 \text{ will liberate } \frac{22.4}{100} \times 5.5 \text{ litres of CO}_2 \text{ at N.T.P.}$$

$$= 1.232 \text{ litres of CO}_2 \text{ at N.T.P.}$$

$$\therefore \text{Total volume of CO}_2 \text{ liberated from 10 gm. of the mineral}$$

$$= 1.12 + 1.232$$

$$= 2.352 \text{ litres at N.T.P.}$$

Since the experiment is performed at 15°C and 745 mm. pressure, the above volume has to be reduced to required conditions by applying the

gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_N V_N}{T_N}$$

$$V_1 = ?$$

$$P_1 = 745 \text{ mm.}$$

$$T_1 = 273 + 15 = 288^\circ \text{A}$$

$$V_N = 2.352 \text{ litres}$$

$$P_N = 760 \text{ mm.}$$

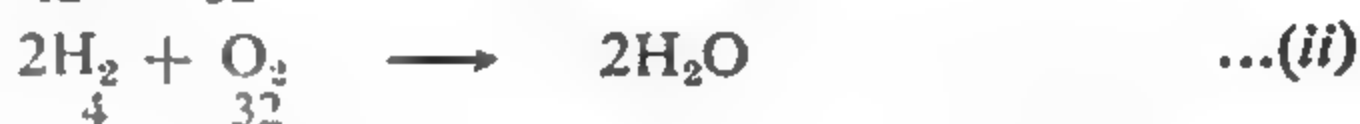
$$T_N = 273^\circ \text{A}$$

$$\text{Thus, we have } \frac{V_1 \times 745}{288} = \frac{2.352 \times 760}{273}$$

$$\therefore V_1 = \frac{2.352 \times 760}{745} \times \frac{288}{273} = 2.531 \text{ litres.}$$

Example 11. Assuming that air contains 23% by wt. of oxygen, find out the volume of air at 27°C and 750 mm. pressure that would be required for the complete combustion of 1 kgm. of coal containing 90% carbon and 5% hydrogen (Density of air = 14.4)

The equations involved are



1 kgm. of coal contains 900 gm. of carbon and 50 gm. of hydrogen. (\therefore %ages of carbon and hydrogen in the coal are 90 and 5 respectively)

According to equation (i),

Wt. of oxygen required for combustion of 900 gm. of carbon
 $= \frac{32}{12} \times 900 = 2400 \text{ gm.}$, and according to the equation (ii),

Wt. of oxygen required for combustion of 50 gm. of hydrogen

$$= \frac{32}{4} \times 50 = 400 \text{ gm.}$$

$$\therefore \text{Total wt. of oxygen required} = 2400 + 400 = 2800 \text{ gm.}$$

\therefore Since air contains 23% by weight of oxygen,

\therefore Wt. of air containing 2800 gm. of oxygen

$$= \frac{100}{23} \times 2800 \text{ gm.} \\ = 12170 \text{ gms.}$$

Now it is known that 1 litre of hydrogen at N.T.P. weighs 0.09 gm. and it is given that the density of air is 14.4.

$$\therefore \text{Wt. of 1 litre of air at N.T.P.} = 14.4 \times 0.09 \\ = 1.296 \text{ gm.}$$

∴ Volume of air at N.T.P. weighing 12170 gm.

$$= \frac{1}{1.296} \times 12170 \text{ litre}$$

$$= 9390.43 \text{ litres.}$$

This volume when reduced to experimental conditions of temperature and pressure will be

$$= \frac{9390.43 \times 760}{273} \times \frac{300}{750}$$

$$= 10456.73 \text{ litres}$$

III. Problems based on Volume relations in Chemical Equations.

Example 12. Calculate the volume of oxygen at 27°C and 750 mm. pressure required for complete combustion of 20 c.c. of ethylene (C₂H₄).

The reaction involved is



By converse of Avogadro's hypothesis, viz., equal number of molecules of all gases will be contained in equal volumes under similar conditions of temperature and pressure, we have

1 vol. of ethylene requires 3 vols. of oxygen at N.T.P.

∴ 200 c.c. of ethylene requires 600 c.c. of oxygen at N.T.P.

Now reducing this volume to required conditions by the gas equation

$$\frac{P_1 V_1}{T_1} = \frac{P_N V_N}{T_N}$$

$$V_1 = ?$$

$$P_1 = 750 \text{ mm.}$$

$$T_1 = 273 + 27 = 300^\circ \text{A}$$

$$V_N = 600 \text{ c.c.}$$

$$P_N = 760 \text{ m.m.}$$

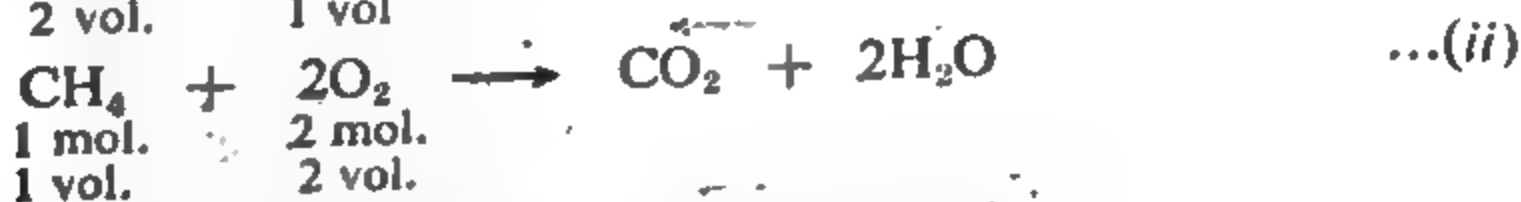
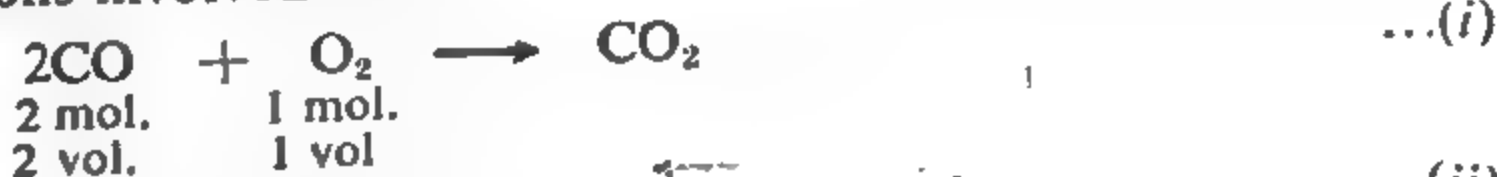
$$T_N = 273^\circ \text{A}$$

$$V_1 = \frac{600 \times 760}{273} \times \frac{300}{750}$$

$$= 66.83 \text{ c.c.}$$

Example 13. Calculate the percentage composition by volume of a mixture of carbon monoxide and methane, 10.5 c.c. of which require 9 c.c. of oxygen for complete combustion.

The reactions involved are



Let 10.5 c.c. of the mixture contain x c.c. of methane.

∴ Volume of CO in the mixture = (10.5 - x) c.c.

According to equation (i),

2 vols. of carbon monoxide require 1 vol. of oxygen for complete combustion.

$\therefore (10.5 - x)$ c.c. of carbon monoxide would require $\frac{(10.5 - x)}{2}$ c.c. of oxygen.

According to equation (ii),

1 vol. of methane requires 2 vols. of oxygen for combustion.

$\therefore x$ c.c. of methane would require $2x$ c.c. of oxygen.

Hence total volume of oxygen required

$$= \frac{10.5 - x}{2} + 2x$$

$$= \frac{10.5 - x + 4x}{2} = \frac{10.5 + 3x}{2}$$

Actually, the vol. of oxygen used $= 9$ c.c.

$$\therefore \frac{10.5 + 3x}{2} = 9$$

$$\text{or } 10.5 + 3x = 18$$

$$\text{or } 3x = 18 - 10.5 = 7.5$$

$$x = \frac{7.5}{3} = 2.5 \text{ c.c.}$$

Hence, volume of methane $= 2.5$ c.c.

Volume of CO $= 10.5 - 2.5 = 8$ c.c.

%age composition by volume :

$$\% \text{age of CO} = \frac{8}{10.5} \times 100 = 76.2$$

$$\% \text{age of CH}_4 = 100 - 76.2 = 23.8$$

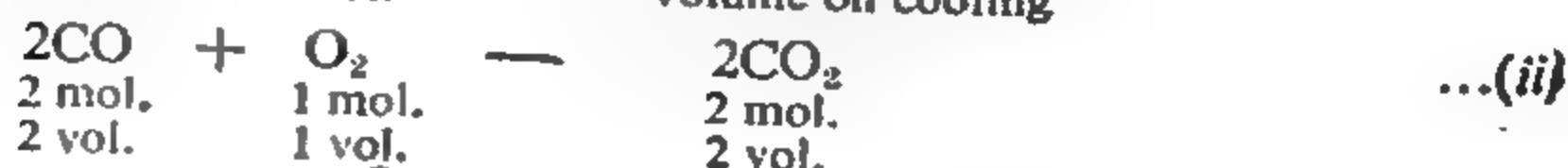
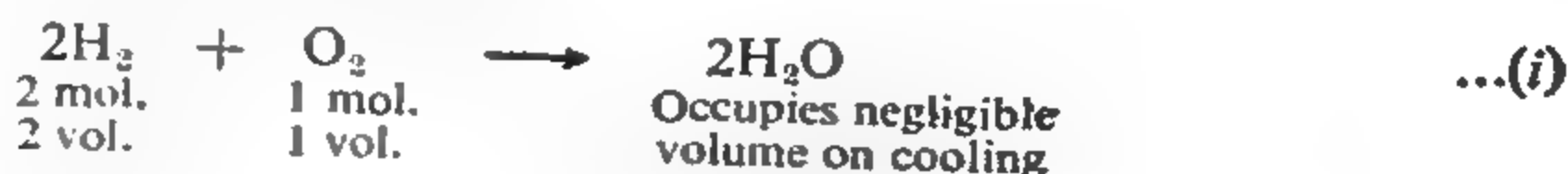
Example 14. 20 volumes of a mixture of hydrogen gas and carbon monoxide were mixed with 13 volumes of oxygen and the mixture exploded. On cooling, the resulting volume was found to be 9. Determine the composition of the mixture.

Vol. of mixture $= 20$ vol.

Vol. of oxygen taken $= 13$ vol.

Vol. of gases after explosion
and cooling $= 9$ vol.

The reactions involved are :



Let the mixture contain x vol. of hydrogen.

$$\therefore \text{vol. of CO} = (20-x) \text{ vol.}$$

According to equation (i), x vol. of hydrogen will need $x/2$ vol. of oxygen and the resulting water occupies negligible volume.

$$\begin{aligned} \therefore \text{The contraction} &= \text{vol. of hydrogen consumed} + \text{vol. of oxygen used up} \\ &= x + x/2 \text{ vols.} \end{aligned} \quad \dots(iii)$$

And according to equation (ii), $(20-x)$ vols. of CO consume $\left(\frac{20-x}{2}\right)$ vol. of oxygen to produce $(20-x)$ vol. of CO_2 .

$$\begin{aligned} \therefore \text{The contraction} &= \text{vol. of carbon monoxide consumed} + \text{vol. of oxygen used up} - \text{vol. of carbon dioxide formed} \\ &= (20-x) + \left(\frac{20-x}{2}\right) - (20-x) \text{ vols.} \\ &= \frac{20-x}{2} \text{ vols.} \end{aligned}$$

$$\text{Hence, total contraction should be} = \frac{3x}{2} + \frac{20-x}{2} \text{ vols.}$$

$$\text{But actually the contraction} = 20 + 13 - 9 = 24 \text{ vols.}$$

$$\therefore \frac{3x}{2} + \frac{20-x}{2} = 24$$

$$\text{whence} \quad x = 14$$

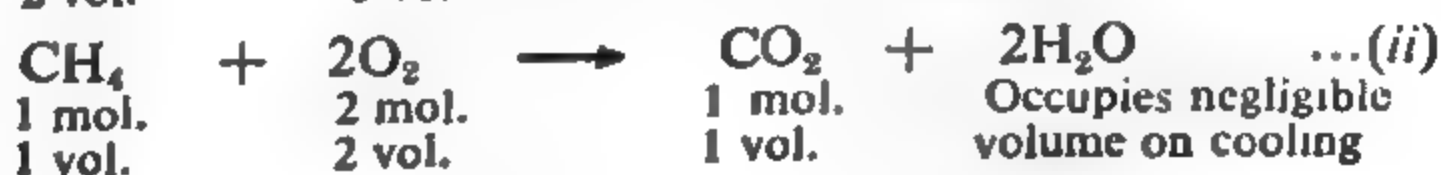
$$\therefore \text{Hydrogen} = 14 \text{ vols.}$$

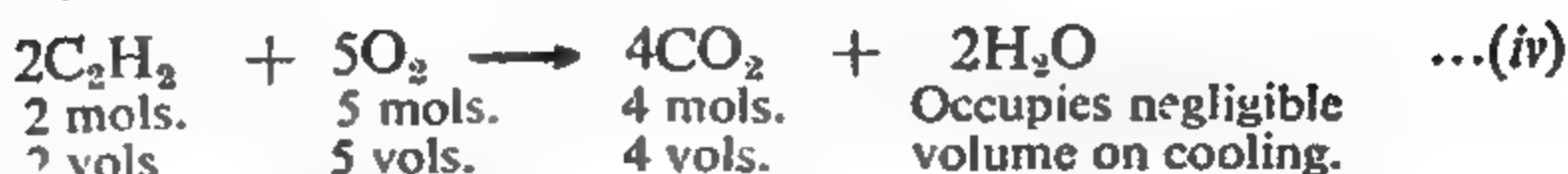
$$\text{and Carbon monoxide} = 20 - 14 = 6 \text{ vols.}$$

Example 15. A sample of coal gas was found to contain 40% hydrogen, 35% methane, 15% carbon monoxide and 10% acetylene. 100 volumes of this gas were mixed with 600 volumes of air (containing 21% oxygen) in an eudiometer tube and exploded. Calculate the volume and composition of the resulting mixture on cooling.

As 100 volume of coal gas is taken, hence according to the percentages given, there will be 40, 35, 15 and 10 vols. respectively of hydrogen, methane, carbon monoxide and acetylene.

On explosion with air, the following reactions will take place :





According to equation (i), volume of oxygen used for complete combustion of 40 vols. of hydrogen
 $= \frac{1}{2} \times 40 = 20 \text{ vols.} \dots(a)$

Similarly, from equation (ii), volume of oxygen used for complete combustion of 35 vols. of methane is
 $= 2 \times 35 = 70 \text{ vols.} \dots(b)$

From equation (iii), volume of oxygen used for 15 vols. of carbon monoxide is
 $= \frac{15}{2} = 7.5 \text{ vols.} \dots(c)$

And from equation (iv), volume of oxygen required for 10 vols. of acetylene
 $= \frac{5}{2} \times 10 = 25 \text{ vols.} \dots(d)$

\therefore Total volume of oxygen required for complete combustion of various gases from (a), (b), (c), and (d)
 $= 20 + 70 + 7.5 + 25$
 $= 122.5 \text{ vols.}$

Now volume of air taken = 600 vols.

Vol. of oxygen present in 600 vols. of air

$$= \frac{21}{100} \times 600 = 126 \text{ vols.}$$

\therefore Vol. of oxygen left unused = $126 - 122.5$
 $= 3.5 \text{ vols.} \dots(v)$

and vol. of nitrogen present at the end

$$= 600 - 126 = 474 \text{ vols.} \dots(vi)$$

From the above equations it is evident that CO_2 is produced during explosion in reactions (ii), (iii) and (iv) which can be calculated easily.

Vol. of CO_2 produced by complete combustion of 35 vol. of methane from reaction (ii) = 35 vols.

Similarly, volume of CO_2 produced by complete combustion of 15 vols of CO from reactions (iii) = 15 vols.

and volume of CO_2 produced by the complete combustion of 10 vols. of acetylene, from reaction (iv) = $\frac{4}{2} \times 10 = 20 \text{ vols.}$

\therefore Total volume of CO_2 produced = $35 + 15 + 20$
 $= 70 \text{ vols.} \dots(vii)$

Hence, the total volume of gaseous mixture after explosion

$$\begin{aligned}
 &= \text{Vol. of O}_2 \text{ left unused} + \text{Vol. of nitrogen} + \text{Vol. of CO}_2 \text{ produced} \\
 &= 3.5 + 474 + 70 \\
 &= 547.5 \text{ vols.}
 \end{aligned}$$

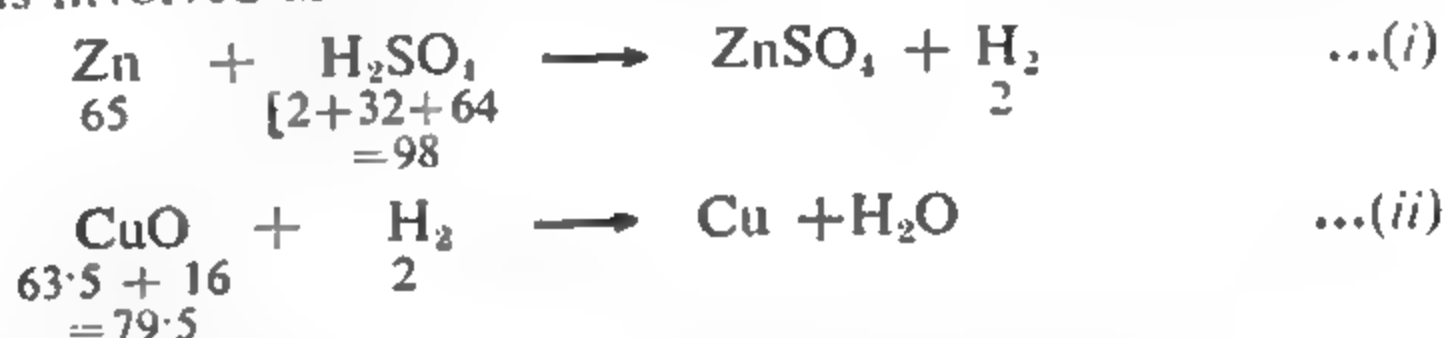
and the composition of the mixture by volume is :

$$\begin{aligned}
 \text{O}_2 &= 3.5 \text{ vols.} \\
 \text{N}_2 &= 474 \text{ vols.} \\
 \text{CO}_2 &= 70 \text{ vols.}
 \end{aligned}$$

(IV) Problems Based on Successive Reactions.

Example 16. What weight of zinc and sulphuric acid would be required to produce enough hydrogen to reduce completely 8.5 gm. of copper oxide to copper ?

The reactions involved are



From equations (i) and (ii),

$$65 \text{ gm. of zinc} \equiv 2 \text{ gm. of hydrogen} \equiv 79.5 \text{ gm. of CuO}$$

\therefore Amount of zinc required to produce enough hydrogen to reduce 8.5 gm. of copper oxide

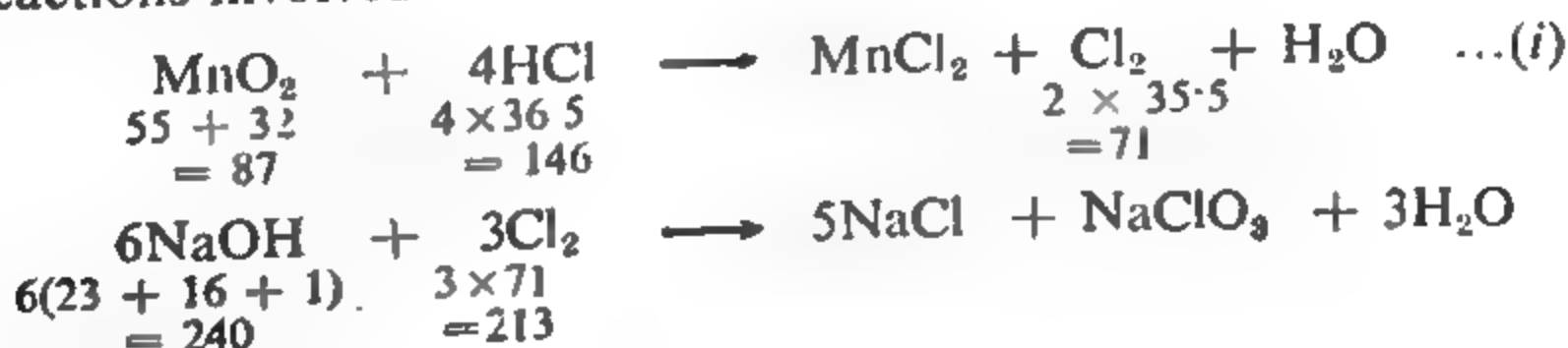
$$= \frac{65}{79.5} \times 8.5 = 6.95 \text{ gm.}$$

and amount of sulphuric acid required for above

$$= \frac{98}{79.5} \times 8.5 = 10.47 \text{ gm.}$$

Example 17. 50 gm. of caustic soda was completely converted into sodium chlorate and sodium chloride by the action of chlorine. What weight of manganese dioxide and what volume of hydrochloric acid (containing 300 gm. of the acid per litre) were used for the production of necessary chlorine ?

The reactions involved are



From equations (i) and (ii)



\therefore 240 gm. of caustic soda (NaOH) $\equiv 3 \times 87$ gm. of MnO_2

or Wt. of MnO_2 required to produce enough chlorine to convert completely 50 gm. of caustic soda into chlorate and chloride

$$= \frac{3 \times 87}{240} \times 50 = \frac{261}{240} \times 50 = 54.875 \text{ gm.}$$

Wt. of hydrochloric acid required

$$= \frac{3 \times 146}{240} \times 50 = 91.25 \text{ gm.}$$

Since hydrochloric acid contains 300 gm. of acid per litre, volume of hydrochloric acid required

$$= \frac{1000}{300} \times 91.25 = 304.167 \text{ c.c.}$$

(V) Problems Based on Volumetric Analysis.

In volumetric analysis, the solution of one substance is made to react with the solution of another under carefully controlled conditions. Since the main emphasis, in this type of analysis, is on volumes of reacting substances, the name **volumetric analysis** is given.

One of the two solutions is usually called a **standard solution**. A standard solution is one whose **strength** is known.

The **strength** of a solution is *the amount of solute (expressed in terms of the number of grams or gram-equivalents) present per litre of the solution*. When expressed in the latter way, the solution is called a **normal solution** or a **decinormal** or a **binormal** solution or **five normal** solution, depending upon if a gram-equivalent or $\frac{1}{10}$ gm. equivalent or $\frac{1}{2}$ gm. equivalent or five times the gram-equivalent weight of the substance is dissolved in one litre of the solution concerned. The same idea is conveyed by stating that the **normality** of the solution is 1 or $\frac{1}{10}$ (0.01) or $\frac{1}{2}$ (0.5) or 5.

Thus, the normality of the solution may be defined as the *factor* with which gram-equivalent has to be multiplied in order to express the strength of the solution. We have, therefore, the important relation :

$$\text{Strength} = \text{Normality} \times \text{Equivalent weight}$$

Since one equivalent of a substance exactly reacts with (or neutralizes) one equivalent of another substance (*law of equivalent weights*), it will be evident that

$$N_1 V_1 = N_2 V_2$$

where N_1 , V_1 and N_2 , V_2 pertain to the normality and volumes of the two solutions respectively. This is the second fundamental relation used in all volumetric analyses and is known as **normality equation**.

There are two more relations frequently used in acid-alkali titrations.* These relations are

$$\begin{aligned} \text{Mol. wt. of an acid} &= \text{Eq. wt. of the acid} \times \text{its basicity} \\ \text{and} \quad \text{Mol. wt. of a base} &= \text{Eq. wt. of the base} \times \text{its acidity} \end{aligned}$$

where *basicity* (or *acidity*) of the *acid* (or *base*) is the *number of replaceable hydrogen atoms* (or *hydroxyl groups*) present in *one molecule* of the *acid* (or *base*).

Example 18. Calculate the number of grams required to make a normal solution of each of the following substances : (i) Na_2CO_3 (ii) NaOH (iii) H_2SO_4 (iv) CH_3COOH .

(1) Sodium carbonate, Na_2CO_3 , reacts with HCl according to the following equation :



106 gms. (1 gm. mol.) of sodium carbonate react with 73 gms. (2 gm. moles or 2 gm. equivalents) of hydrochloric acid. Therefore, 1 gm. equiv. of hydrochloric acid reacts with $106/2 = 53$ gms. of Na_2CO_3 or the gm. equiv. of Na_2CO_3 is 53 gms.

Hence, 1 normal solution of Na_2CO_3 must contain 53 gms. per litre of Na_2CO_3 .

(2) Sodium hydroxide, NaOH , contains one replaceable hydroxyl group or its acidity is one.

Therefore, equivalent wt. of $\text{NaOH} =$ its mol. wt. viz., 40.

Hence, a normal solution of NaOH should contain 40 gms. per litre of it.

(3) Sulphuric acid, H_2SO_4 is a *dibasic* acid as it contains two replaceable hydrogen atoms. Therefore, its equiv. weight is one-half of its molecular weight.

Hence, number of grams of sulphuric acid which must be present in its normal solution is 49 ($=98/2$).

(4) Acetic acid, CH_3COOH , is a *monobasic* acid. Thus, its equivalent weight will be equal to its molecular weight. Therefore, the number of grams required to make a normal solution of acetic acid is 60.

Example 19. Calculate the normality of the following solutions :

- A solution of sulphuric acid containing 4.9 gms./litre.
- A solution of sodium hydroxide containing 8.0 gms./litre.
- A solution of sodium carbonate containing 13.25 gms./litre.

* The process of neutralisation of one solution with another is called a titration. Where one of the solutions is an acid and the other is a base, the titration is named acid-alkali titration.

$$(i) \quad \text{Eq. wt. of } \text{H}_2\text{SO}_4 = \frac{\text{Mol. wt.}}{2} = 49$$

$$\text{Normality} = \frac{\text{Strength}}{\text{Eq. wt.}} = \frac{4.9}{49} = \frac{1}{10} \text{ or } 0.1$$

$$(ii) \quad \text{Eq. wt. of NaOH} = \text{Mol. wt.} = 40$$

$$\text{Normality} = \frac{\text{Strength}}{\text{Eq. wt.}} = \frac{8.0}{40} = \frac{1}{5} \text{ or } 0.2$$

$$(iii) \quad \text{Eq. wt. of } \text{Na}_2\text{CO}_3 = \frac{\text{Mol. wt.}}{2} = 53$$

$$\text{Normality} = \frac{\text{Strength}}{\text{Eq. wt.}} = \frac{13.25}{53} = \frac{1}{4} \text{ or } 0.25$$

Example 21. 300 ml. of NaOH solution of unknown strength contains as much alkali as 50 ml. of another NaOH solution containing 6 gms. of NaOH per litre. Calculate the strength and normality of the unknown NaOH solution.

Strength of the second NaOH solution = 6 gms. per litre

Amount of NaOH present in 50 ml. = $\frac{6}{1000} \times 50 = 0.3$ gm.

Since 300 ml. of first NaOH also contain 0.3 gm. of NaOH,

\therefore Strength of the first NaOH solution = $\frac{0.3}{300} \times 1000 = 1$ gm./litre

\therefore Normality of the first solution = $\frac{\text{Strength}}{\text{Eq. wt.}}$
 $= \frac{1}{40} = 0.025$

Example 22. If 25 ml. of N H_2SO_4 neutralized 21 ml. of a solution of sodium carbonate, calculate the strength of sodium carbonate solution.

Volume of H_2SO_4 taken = 25 ml. (V_1)

Normality of H_2SO_4 = 1.0 (N_1)

Volume of Na_2CO_3 neutralised = 21.0 ml. (V_2)

Normality of Na_2CO_3 solution = N_2

Applying the normality equation

$$N_1 V_1 = N_2 V_2$$

$$1.0 \times 25 = N_2 \times 21.0$$

$$N_2 = \frac{1.0 \times 25}{21.0} = 1.1905$$

\therefore Strength of Na_2CO_3 solution = Eq. wt. \times normality
 $= 53 \times 1.1905$
 $= 63.0965$ gms./litre.

Example 23. 0.75 gm. of an acid of Mol. wt. 90 required 16.6 ml. of $N\text{NaOH}$ for neutralisation. Calculate the basicity of the acid.

$$16.6 \text{ ml. of } N \text{ NaOH} \equiv 0.75 \text{ gm. of the acid}$$

$$1000 \text{ ml. of } N \text{ NaOH} = \frac{0.75}{16.6} \times 1000 \text{ gm.}$$

$$= 45.18 \text{ gm. of the acid}$$

$$\text{Since 1 gm. equiv. of NaOH} \equiv 1 \text{ gm. equiv. of acid}$$

$$\text{Eq. wt. of acid} = 45.18$$

$$\text{Mol. wt. of acid} = 90$$

$$\text{Basicity} = \frac{\text{Mol. wt.}}{\text{Eq. wt.}} = \frac{90.00}{45.18} = 1.99$$

$$= 2 \text{ (being the nearest whole number)}$$

Example 24. 0.125 gm. of a sample of limestone was dissolved in 30 ml. of $N/10 \text{ HCl}$ and the solution was then made up to 100 ml. 10 ml. of the diluted solution required for neutralisation 1.5 ml. of $N/20 \text{ NaOH}$. Calculate the percentage of CaCO_3 in limestone.

$$\text{Wt. of the impure limestone taken} = 0.125 \text{ gm.}$$

$$\text{Volume of } \frac{N}{10} \text{ HCl taken} = 30 \text{ ml.}$$

$$\text{Volume of excess (unneutralised) acid was diluted up to 100 ml.}$$

$$10 \text{ ml. of the diluted acid solution of normality } N_1$$

$$\equiv 1.5 \text{ ml. of } \frac{N}{20} \text{ NaOH solution}$$

$$\therefore N_1 \text{ (normality) of the diluted acid} = \frac{1.5}{10} \times \frac{1}{20}$$

$$= 0.0075$$

$$\text{Now 100 ml. of } 0.0075 \text{ N diluted acid} = V \text{ ml. of } \frac{N}{10} \text{ acid.}$$

$$V = 100 \times 0.0075 \times 10$$

$$= 7.5 \text{ ml.}$$

$$\begin{aligned} \text{Thus, volume of } \frac{N}{10} \text{ HCl used up for neutralisation of 0.125 gms. of} \\ \text{the impure sample of } \text{CaCO}_3 &= 30 - 7.5 \\ &= 22.5 \text{ ml.} \end{aligned}$$

Now, weight of CaCO_3 which reacted with 22.5 ml. of $\frac{N}{10} \text{ HCl}$ can be calculated as below :

$$\text{Since 1000 ml. of } N \text{ HCl} \equiv 50 \text{ gm. of } \text{CaCO}_3$$

$$22.5 \text{ ml. of } \frac{N}{10} \text{ HCl} = \frac{50}{1000} \times \frac{1}{10} \times 22.5$$

$$= 0.1125 \text{ gm.}$$

$$\therefore \text{Percentage of CaCO}_3 = \frac{0.1125}{0.125} \times 100 = 90\%$$

QUESTIONS

(a) Weight—Weight Relationship.

1. Calculate the quantity of lime (CaO) required to soften 60,000 litres of temporary hard water containing 16.2 gm. of calcium bicarbonate per hundred litres.
(Ans 3360 gms) (*Panjab Inter 1953*)
 2. In order to find the strength of a sample of sulphuric acid, 10 grams were diluted with water and a piece of marble weighing 7 gms. placed in it. When all action had ceased the marble was removed, washed, dried and was found to weigh 2.2 gm. What was the percentage strength of the acid?
(Ans. 47.04) (*Delhi Pre-medical 1950*)
 3. A sample of commercial sodium chloride (common salt) was analysed. 3.6 gm. of the sample gave with silver nitrate 7.74 gm of dried silver chloride. What is the percentage of impurities in the commercial stuff taking into consideration that all the impurities are in the form of the chloride of potassium?
(Ans. 695.8%) (*Rajputana Inter 1947*)
 4. One gm. of a mixture of potassium chloride and sodium chloride on treatment with excess of silver nitrate gave two gm. of silver chloride. What was the proportion of the two salts in original mixture?
(Ans. 6.14 : 1) (*Panjab Inter 1955 S*)
 5. A certain weight of sodium iodide and sodium chloride mixture when treated with sulphuric acid was found to give the same weight of sodium sulphate. Calculate the percentage composition of the mixture.
(Ans. NaI=28.85 NaCl=71.15) (*Punjab Inter 1952 S*)
 6. A mixture of cuprous oxide and cupric oxide was found to contain 88% of copper. Using 64 as the at. wt. of copper, calculate the percentage of the two components in the mixture.
(Ans. Cu₂O—90% CuO=10%) (*Nagpur Inter 1952*)
 7. A mixture of calcium carbonate and magnesium carbonate weighing 1.42 gm. was strongly heated until no loss of weight was perceived. The residue weighed 0.76 gm. What percentage of the mixture was MgCO₃?
(Ans. 29.38%) (*U.P. Board Inter 1953*)
 8. Assuming that in the process of manufacture of sulphuric acid from iron pyrites only 90% of sulphur present in the ore is converted into sulphuric acid, calculate the weight of this ore necessary for the manufacture of 4 tons of the acid.
(Ans. 3.4 ton) (*Patna Inter. 1953*)
- (b) Weight—Volume Relationship.
9. How many c.c. of nitric acid (strength 56% by wt.) are required to oxidise 10 gm. of ferrous ammonium sulphate (Mol. Wt. 392) assuming HNO₃ to decompose the way $2\text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2\text{NO} + 3\text{O}$.
(Ans. 0.95 c.c.) (*U.P. Board Inter 1949*)
 10. 2.5 gm. of potassium chlorate on heating gave 580 c.c. of oxygen at 17°C and 750 mm. pressure. Assuming the decomposition to be complete, calculate the percentage purity of the sample.
(Ans. 78.56) (*Panjab Inter 1947*)
 11. 1.4 gm. of a sample of chalk (CaCO₃) containing clay as an impurity was treated with an excess of dilute HCl. The volume of the resulting gas at 15°C and 767 mm. pressure was 282 c.c. Calculate the percentage purity of the sample.
(Ans. 86) (*Delhi Prep 1950*)
 12. 0.0327 gram of an impure sample of aluminium gave on treatment with dilute hydrochloric acid 39.3 c.c. of moist hydrogen measured at 13°C and 761 mm. pressure. The impurity in the sample was alumina. Calculate the percentage purity of the metal (Aqueous tension at 13°C = 11 mm.)
(Ans. 92.66) (*Cal. Inter 1946*)
 13. 10 c.c. of liquid carbon disulphide (specific gravity on absolute scale 2.63) are burnt in oxygen according to the equation $\text{CS}_2 + 3\text{O}_2 \rightarrow \text{CO}_2 + 3\text{SO}_2$. Find out the

volume of oxygen necessary to burn this liquid and the volume of resulting gases measured at N.T.P. (Ans. 23.254 litres, 31.00 litres) (*Panjab Inter 1956*)

14. In a certain experiment 13 litres of carbon dioxide at 27°C and 765 mm. pressure are required. How much marble of 96% purity would be required to prepare the above quantity of the gas at the experimental conditions? (Ans. 42.39 gm) (*U.P. Board Inter 1954*)

15. What weight of KMnO_4 and what volume of HCl (Sp. gravity 1.212) would be required to produce 8.0 litres of chlorine at 15°C and 759 mm. pressure? (Ans. $\text{KMnO}_4 = 21.33 \text{ gm.}$; $\text{HCl} = 3252 \text{ c.c.}$) (*Panjab Inter 1957*)

16. 1.60 gm. of a sample of ammonium sulphate on treatment with an excess of sodium nitrite solution liberated 760 c.c. of dry nitrogen at 0°C and 748 mm. pressure. Find the percentage purity of ammonium sulphate. (Ans. 82.5) (*Panjab Inter 1954*)

17. Calculate the maximum weight of iron oxide obtained when one litre of steam at 100°C and 760 m.m. pressure is passed over red hot iron. (Ans. 1.895 gm.) (*Patna Inter 1954*)

18. Assuming that air contains 21 per cent of oxygen by volume, calculate the volume of air 27°C and 756 mm. pressure that will be required for complete combustion of 1.6 gm. of a hydrocarbon containing 75% of carbon and 25% of hydrogen by weight. (Ans. 23.57 litres) (*Madras Inter 1949*)

19. A balloon of capacity 112 litres is to be filled with hydrogen at a temperature of 27°C and a pressure equal to 8.8 metres of mercury. If the hydrogen has to be produced by the action of steam on iron, calculate how much pure iron will be theoretically required for the purpose. (Ans. 2212.7 gms.) (*Jammu & Kashmir Inter 1953*)

20. 44 gm. of an impure sample of the iron sulphide when treated with excess of dilute sulphuric acid gave 5.831 litres of sulphuretted hydrogen at 15°C and 773 mm. pressure. Calculate the percentage purity of the sample of iron sulphide. (Ans. 49.9%) (*Delhi Prep. 1948*)

(c) Volume—Volume Relationship.

21. 20 c.c. of a mixture of carbon monoxide and acetylene on firing with 30 c.c. oxygen occupies 34 c.c. which leaves behind 8 c.c. of residual oxygen after treatment with caustic potash. What was the composition of the original mixture? (Ans. $\text{CO} = 14 \text{ c.c.}$, $\text{C}_2\text{H}_2 = 6 \text{ c.c.}$) (*Ajmer Inter 1952, Rajputana Inter 1958*)

22. 100 c.c. of a gas were completely decomposed with tin, the tin being converted into stannous sulphide. The residual gas consisted of hydrogen and when passed over heated copper oxide gave 0.011 gm. of water. The V.D. of gas is 17. Deduce the formula of the gas. (Ans. H_2S) (*Panjab Inter 1952*)

23. A sample of coal gas contains 50% hydrogen, 30% marsh gas (CH_4), 14% carbon monoxide and 6% ethylene. One hundred cubic centimetres of this gas are mixed with 150 c.c. of oxygen and the mixture exploded. What would be the volume and composition of the resulting gas when cooled to the original temperature? (Ans. Volume = 96 c.c.; 56 c.c. CO_2 and 40 c.c. O_2) (*U.P. 1952*)

24. 10 c.c. of a mixture of methane, ethylene and carbon dioxide were exploded with excess of air. After explosion there was a contraction of 17 c.c. and after treatment with KOH there was a further reduction of 14 c.c. What was the composition of the mixture? (Ans. Methane = 4.5 c.c., Ethylene = 4.0 c.c., $\text{CO}_2 = 1.5 \text{ c.c.}$) (*Madhya Bharat, Inter 1952*)

25. 25 c.c. of a mixture of nitrogen and nitric oxide is passed over ignited copper and the gaseous product is collected and found to occupy 20 c.c. Calculate the percentage composition of the mixture. (Ans. $\text{N}_2 = 60\%$, $\text{NO} = 40\%$) (*Gauhati Inter 1954*)

26. 100 c.c. of a sample of ozonized oxygen was treated with turpentine when the volume was reduced to 70 c.c. If another 100 c.c. of the sample be heated till ozone is decomposed and then cooled to the original temperature and pressure, what volume will the gas occupy? (Ans. 115 c.c.) (*Madras Inter 1946*)

27. 100 ml. of water gas containing some carbon dioxide was exploded with 100 ml. of oxygen and volume after explosion was 100 ml. On introducing sodium hydroxide

great pressure is permitted to expand into a region of low pressure, it suffers a fall in temperature. This phenomenon is known as **Joule-Thomson effect**. This, incidentally, offers further support to the view that attractive forces do exist between gas molecules. As the gas expands, the molecules fall apart from one another. Therefore, work has to be done to overcome the cohesive or attractive forces which tend to hold the molecules together. This work is done at the expense of the kinetic energy of the molecules. Consequently, the kinetic energy decreases and as this is proportional to temperature, cooling results. It may be noted that *no external work is done by the gas in expansion in the present case*.

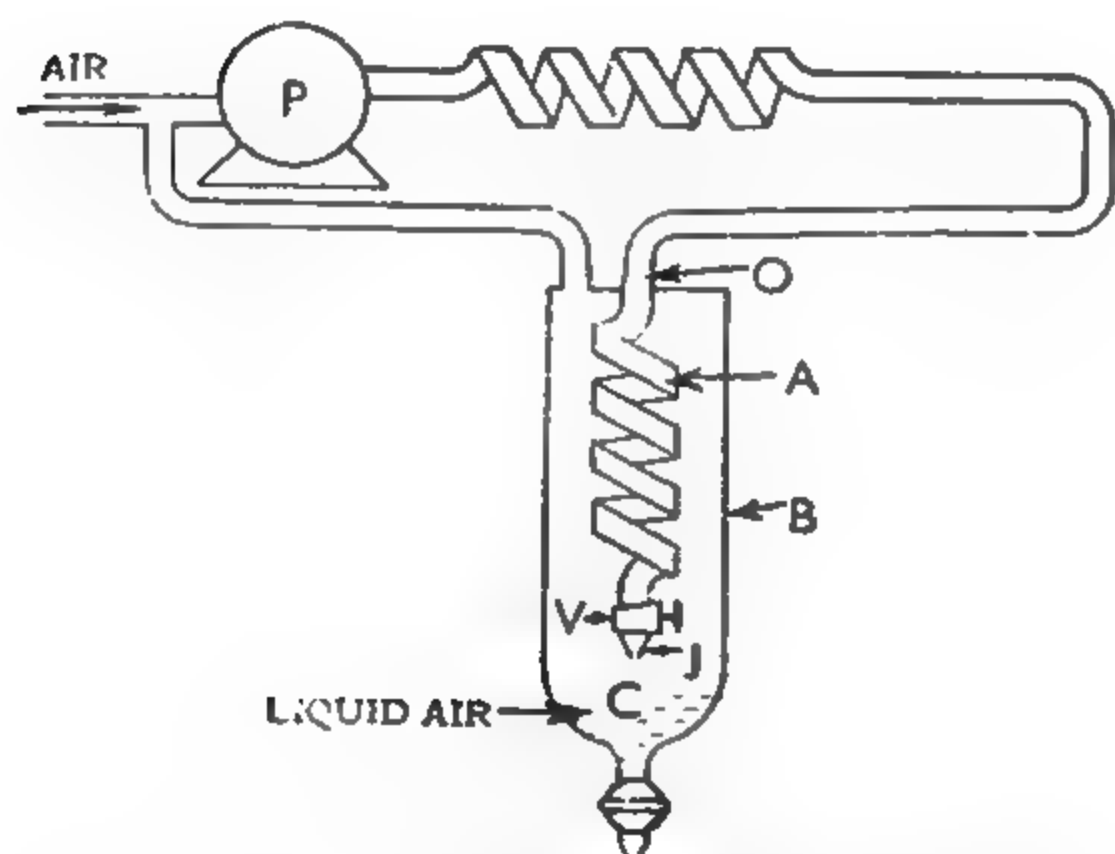


Fig. 9.1. Linde's apparatus for liquefaction of air.

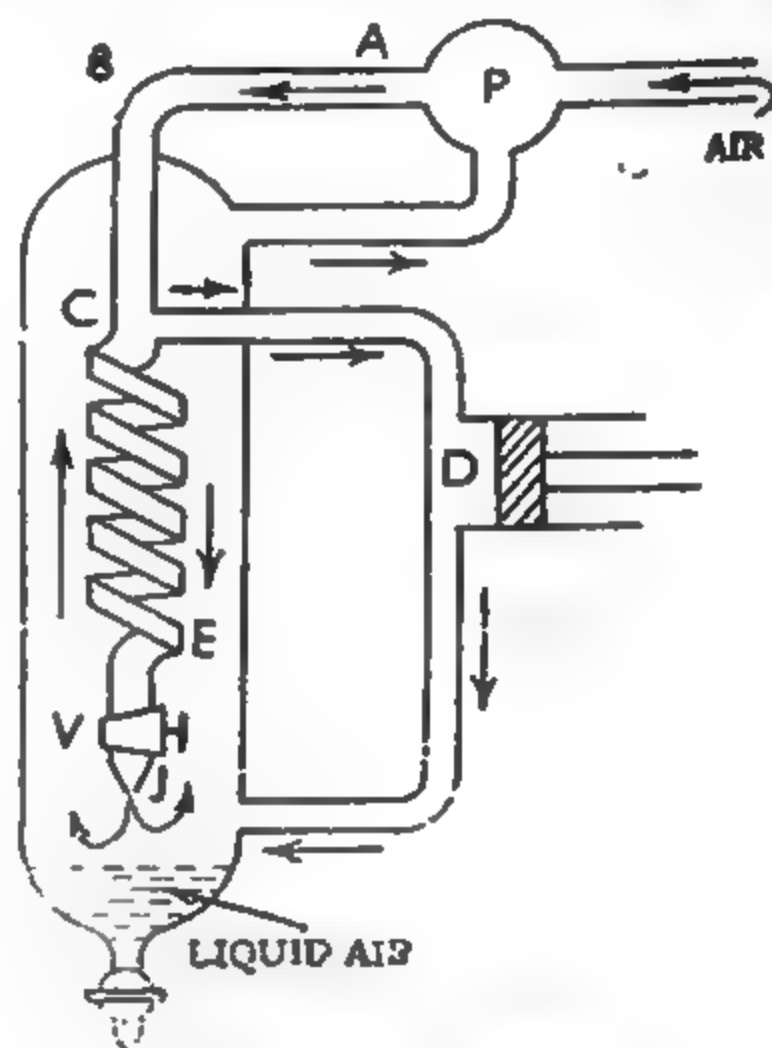


Fig. 9.2. Claude's apparatus for liquefaction of air.

Linde's apparatus which works on this principle is shown in Fig. 9.1. The air, freed of moisture and impurities, is compressed to a high pressure and enters the inner tube of concentric pipes at O, as shown, under a pressure of about 200 atmospheres. The valve V in jet J is then opened to allow it to expand suddenly into the wide chamber C, where it gets cooled. Its pressure at this stage is reduced to about 50 atmospheres. The cooled air is then made to pass through the outer tube B and cools the incoming air passing through the inner tube A. The incoming air, thus, gets further cooled on expansion into the wide chamber C. The air that passed through the apparatus first, is compressed again to 200 atmospheres and made to pass through the inner tube and expand into the chamber C again. This goes on till the liquid air issues from the jet.

(2) **Adiabatic Expansion.*** When a gas is made to expand against a pressure, as in an engine, it does some external work at the expense

*When a system undergoes a change of pressure or volume in such a way that it can neither absorb nor give out heat to the surroundings, the change is said to be adiabatic.

of its kinetic energy which decreases. Hence, there is a fall of temperature.

This principle, combined with Joule Thomson effect, has been used in **Claude's process** for the liquefaction of air.

Air, dried and freed of carbon dioxide, is compressed to about 200 atmospheres and passed through the pipe *ABC*, which bifurcates at *C*, (Fig. 9.2). A part of the air goes into the cylinder *D*, provided with an air-tight piston. There it expands and does *external work* in moving the piston outwards. The temperature of gas, therefore, falls. The cooled air then goes up the chamber *E* and cools the portion of the compressed air passing down the tube *CE*. This chilled gas then passes through a throttle or jet *J* and is further cooled by Joule-Thomson effect. This goes on till the gas changes into liquid.

Industrial preparation of nitrogen and oxygen from liquid air.

On a commercial scale, nitrogen and oxygen are invariably obtained from liquid air by carrying out its fractional evaporation. Nitrogen having a lower boiling point (-195.7°C) boils off more readily than the less volatile oxygen (boiling point -182.96°C).

The plant used for carrying out simultaneously the liquefaction of air and its fractional evaporation, is shown in Fig. 9.3.

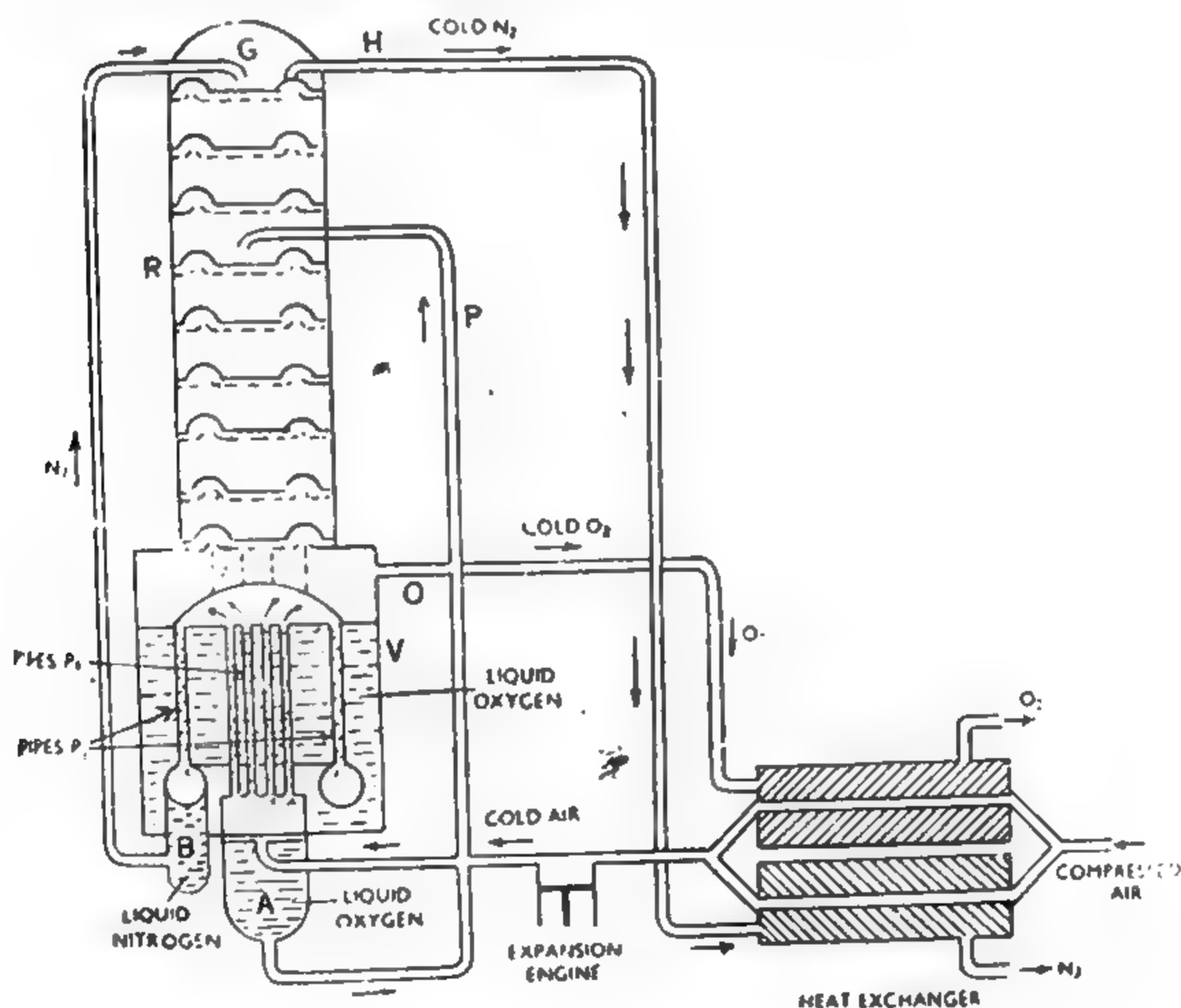


Fig. 9.3. Manufacture of nitrogen and oxygen by fractional evaporation of liquid air.

The air to be liquefied is *thoroughly dried and freed from carbon dioxide* and then compressed to about 30 atmospheres. The heat of compression is eliminated by cooling the air in the heat exchanger cooled by the out-going very cold oxygen and nitrogen. The cold compressed air is then made to do work in the expansion engine, thereby losing an equivalent amount of energy as a result of which its temperature falls to about its liquefaction point. This air then enters the vaporiser V fitted with double set of pipes P_1 and P_2 , dipping in liquid oxygen. As it ascends the inner pipes P_1 , there occurs an exchange of heat between the liquid oxygen and the cooled air. As a result, the oxygen evaporates and the air gets partially condensed. The condensed liquid, which is richer in oxygen, flows down and collects in the vessel, A . While going down the pipes P_1 , it scrubs the upgoing air, as a result of which an exchange of constituents takes place. Consequently, the down-flowing liquid gets richer and richer in oxygen while the upgoing air becomes richer and richer in nitrogen. By properly adjusting the pressure of the air, the gas which escapes the inner pipes is found to be practically pure nitrogen, while the liquid which flows down contains about 50 per cent each of oxygen and nitrogen. It collects in the vessel A at the base of the vaporiser. The escaped nitrogen passes down through the outer pipes, P_2 , gets liquefied and collects in the vessel B .

The liquid in the vessel A is forced upwards under its own vapour pressure, through a pipe P , fitted with a regulating valve, and is admitted into the rectifier R at about its middle. As the liquid flows down, it meets an upward current of oxygen coming from the vaporiser V . In this process the liquid is robbed off its more volatile component, nitrogen, which moves upwards. The ascending nitrogen is further scrubbed by liquid nitrogen admitted at G , near the top of the rectifier from the vessel B , and is thus almost completely freed of oxygen. The nitrogen escaping through H at the top of the rectifier R is thus almost **pure nitrogen**.

The liquid moving downwards is almost completely deprived of nitrogen. It collects in the vaporiser V , where it is made to boil by the heating effect of the air which is admitted into the inner pipes, as discussed earlier. It gives off almost **pure oxygen** gas which is led out of the opening, O , into the heat exchanger. The pure nitrogen issuing at the top of the rectifier also passes through the heat exchanger, as shown.

QUESTIONS

1. Explain the term critical temperature. What is the significance of critical temperature in liquefaction of gases?
2. What principles are involved in cooling gases below their critical temperature? Describe Linde's apparatus for the liquefaction of air.
3. Explain the term Joule-Thomson effect and adiabatic expansion. Describe Claude's apparatus for the liquefaction of air.
4. Describe in details the construction and working of the plant used for the liquefaction of air and its fractionation to prepare nitrogen and oxygen.
5. Explain in details how nitrogen and oxygen are obtained from air, on industrial scale.

CHAPTER X

HYDROGEN AND WATER

HYDROGEN

Hydrogen is the first element in the periodic table. Its atomic number is 1 and atomic weight 1.008. The nucleus of the hydrogen atom contains one proton and no neutron. The atom has one planetary electron arranged in the *K*-shell. It has a tendency to lose this electron when it changes into a hydrogen ion (H^+) or a proton. It has also a tendency to gain one electron to complete the *K*-shell, that is, to attain the configuration of the next inert gas, helium. The additional electron may also be gained covalently.

History. Cavendish, in 1766, while studying the comparative effect of dilute acids on metals like zinc, iron and tin, found that a similar gas was obtained in each case. He called this gas as *inflammable air* since it burnt when ignited. The name hydrogen (Greek, *hydro* - water forming) was given to the gas by Lavoisier who found that the gas when burnt in air produced water.

Occurrence. Hydrogen does not occur free in nature, except for traces (about 1 part in 1.5 million parts) in air and in volcanic regions and in some meteorites. However, solar spectra indicate that sun's atmosphere contains appreciable amounts of hydrogen.

It occurs most commonly in combination with oxygen as water and to a much smaller extent in combination with carbon, sulphur, nitrogen and the halogens. All organic matter, whether of vegetable or animal origin, contains hydrogen in combination with carbon, nitrogen and oxygen.

Preparation.

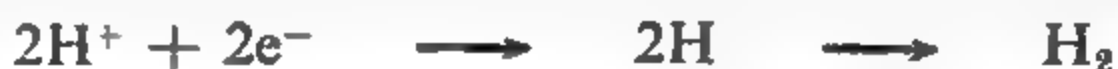
Hydrogen is prepared by the decomposition of its common compounds such as water, acids and alkalies.

The more important methods are briefly described below :

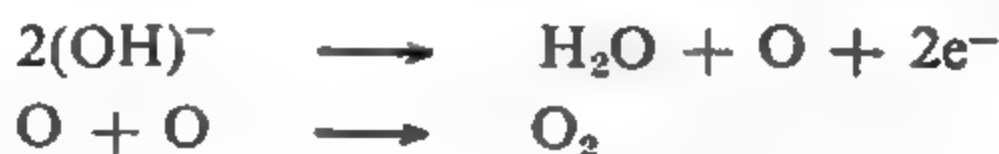
(a) **From Water** (i) **By electrolysis.** When water containing a small amount of acid or alkali is electrolysed, hydrogen is evolved at the cathode and oxygen at the anode:

Suppose water contains sulphuric acid. Then the ions present in the solution are H^+ , SO_4^{--} , and OH^- (furnished by small ionisation of water).

At *cathode*, hydrogen ions are discharged to give hydrogen gas :



At *anode*, hydroxyl ions are discharged to give oxygen gas :



Sulphate ions, although present in much larger quantity, are not discharged, as their **discharge potential is very much higher than that of hydroxyl ions**.

If water to be electrolysed contains an alkali, say potassium hydroxide, then the ions present in the solution are K^+ , OH^- , and H^+ (furnished by small ionisation of water).

At *cathode*, hydrogen ions are discharged and **not** potassium ions as the discharge potential of the latter is very much higher.

At *anode*, hydroxyl ions are discharged to give oxygen, as represented above.

The mechanism of electrolysis of aqueous solution of sulphuric acid is represented in some books as :

At *cathode* :



At *anode* :



This is **incorrect** since SO_4^{--} ions cannot be discharged as long as OH^- ions are present in solution.

Similarly, the mechanism of the electrolysis of aqueous KOH solution, involving the discharge of K^+ ions at the cathode, as given in some books is **incorrect** because K^+ ions cannot be discharged as long as H^+ ions are present in solution.

(ii) **By the action of certain active metals on water.** Alkali metals are the most active for this reaction. For example, when a small piece of sodium is put into cold water, a violent reaction, resulting in the formation of hydrogen, takes place instantaneously :

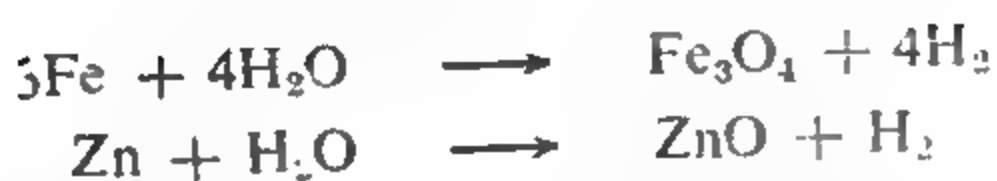


A large amount of heat is given off in the reaction and very often hydrogen evolved catches fire causing a violent explosion.

The reaction between calcium and water is rapid but not violent. The reaction with magnesium takes place only when water is warmed.



Iron and zinc are even less reactive. They decompose water only when super heated steam is led over them at a high temperature.

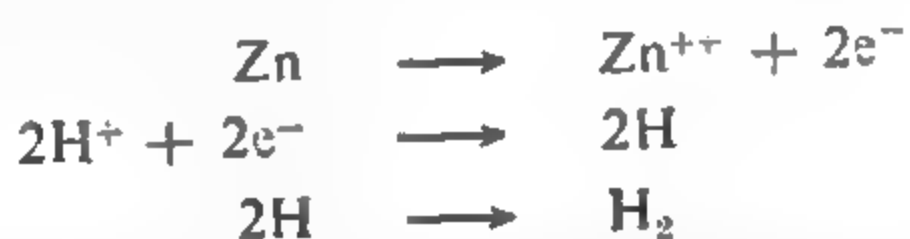


Most other elements are far less reactive to be able to displace hydrogen from water.

(iii) **By the action of water on a metal hydride.** The hydrides of alkali and alkaline earth metals readily give out hydrogen when dissolved in water :



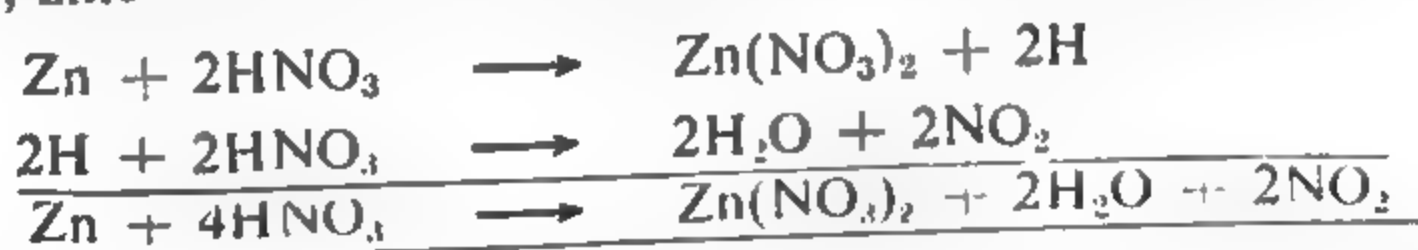
(b) **From Dilute Acids.** Hydrogen is a common constituent of all acids. The mineral acids like HCl , H_2SO_4 and HNO_3 are largely ionised in aqueous solutions into hydrogen ions (H^+) and the acid anions. Metals like zinc, tin and aluminium have strong tendencies to pass into solution as positive ions. In doing so they lose electrons which are gained by the positively charged hydrogen ions which change into neutral hydrogen atoms. The atoms unite to form molecules. The changes are represented as,



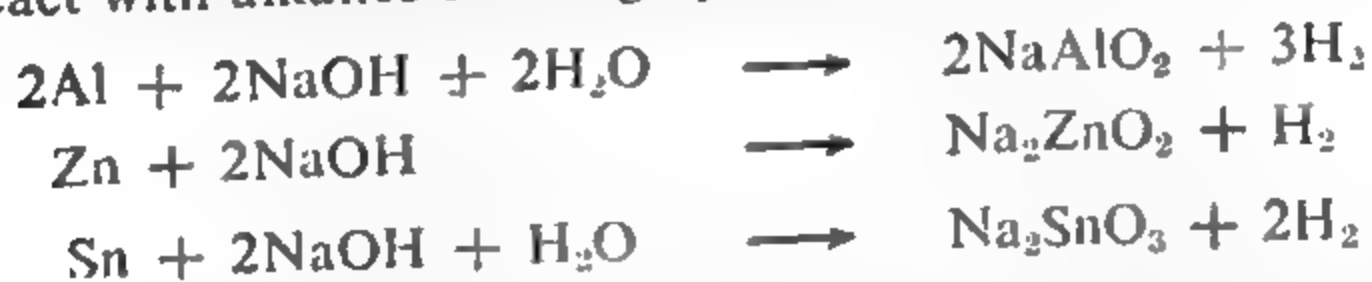
The complete reaction with dilute sulphuric acid, as usually written, is



In case of acids which are also oxidising agents, e.g., nitric acid and concentrated sulphuric acid, the hydrogen produced gets oxidised to water. Thus, zinc with conc. nitric acid gives nitrogen dioxide.



(c) **From Alkalies.** Certain metals like aluminium, zinc and tin react with alkalies evolving hydrogen. Thus,



Preparation of Pure Hydrogen. Pure hydrogen is usually obtained by the electrolysis of a warm concentrated solution of recrystallised barium hydroxide in a hard glass U-tube using nickel electrodes. The gas is passed over heated platinum gauze when oxygen present as an impurity on account of diffusion from the anode is converted into water which is removed on passing the gas over solid caustic potash and phosphorus pentoxide (Fig. 10.1).

The gas is finally absorbed in hot palladium foil from which it can be recovered, in pure state, by raising the temperature to dull red heat.

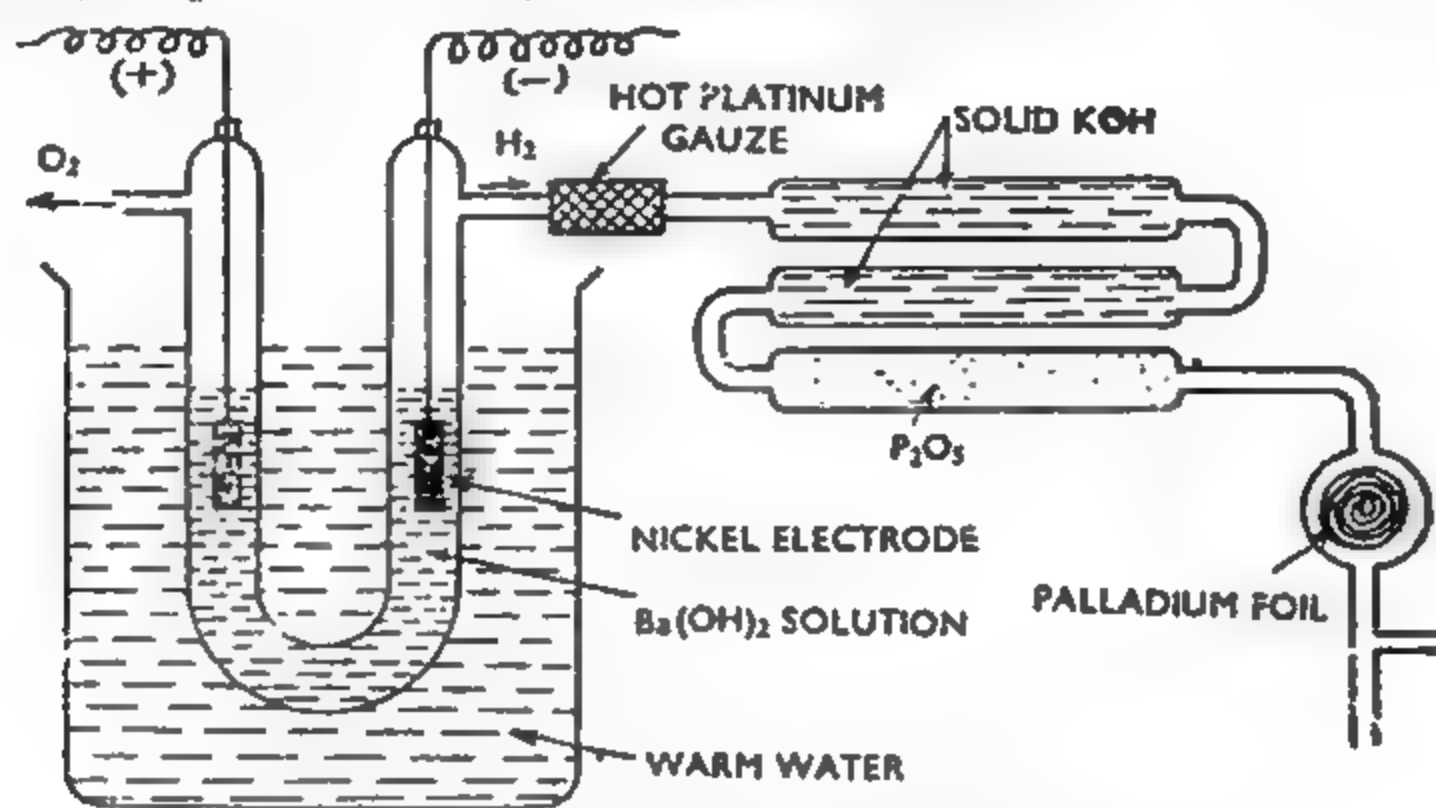


Fig. 10.1. Preparation of pure hydrogen.

Barium hydroxide is preferred to sodium hydroxide since if any carbon dioxide is absorbed, the barium carbonate produced being insoluble settles down and does not interfere with the electrolytic process.

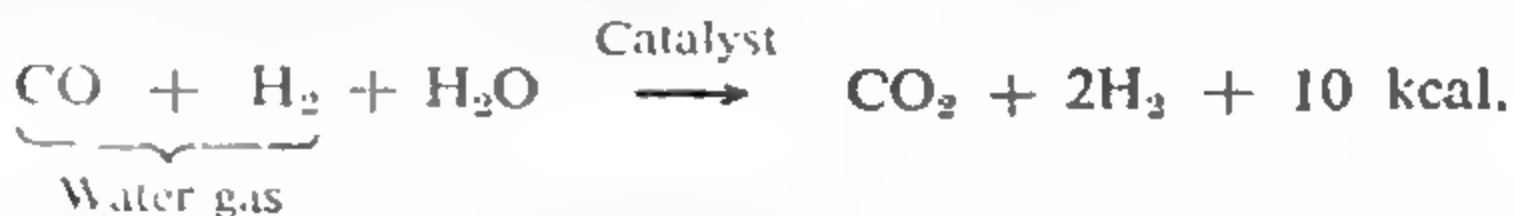
Industrial Preparation of Hydrogen. Water is the main source for the production of industrial hydrogen. The various methods in use are briefly described below :

(i) **By the electrolysis of water.** By the electrolysis of water containing a small quantity (about 15–20%) of sulphuric acid, oxygen is liberated at the anode which is usually nickel-plated and hydrogen at the cathode which is usually made of iron.

(ii) **Bosch process.** This process depends upon the reduction of water vapour (steam) by carbon. When superheated steam is passed over heated coke at temperatures varying from 440° to 600° , a mixture of carbon monoxide and hydrogen (known as water gas) is obtained.



The water gas is made to react again with steam at the same temperature in the presence of a catalyst, usually a mixture of iron, chromium and cobalt, when carbon monoxide is oxidised to carbon dioxide. The reaction is exothermic.



The heat of the reaction is sufficient to maintain the temperature at the required level.

Carbon dioxide is removed by washing with water under a pressure of about 25–30 atmospheres. Any unchanged carbon monoxide, if

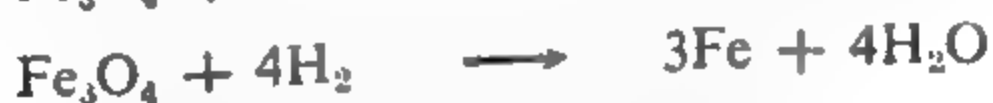
present, is removed by passing through ammoniacal solution of cuprous formate at 200 atmosphere pressure. Water is mostly removed by freezing it out. The last traces are removed by passing over anhydrous copper sulphate or calcium chloride. Hydrogen prepared by this method is used largely in the manufacture of ammonia by Haber process.

(iii) **Lane process.** In this process heated iron is used to reduce steam.

Superheated steam is passed over iron heated to about 900° when hydrogen is produced according to the reaction :



The iron oxide is reduced by passing CO over it to iron which is used over again. Actually, water gas is used for reducing the iron oxide. The following reactions take place :



These reactions also take place at 900° .

In actual process, iron is heated in a tube over a furnace maintained at the required temperature and steam and water gas are led over it alternately, the first for 10—15 minutes and the second for 20—30 minutes.

(iv) **As a by-product in the manufacture of sodium hydroxide.** Sodium hydroxide is prepared on a commercial scale by the electrolysis of aqueous solutions of sodium chloride in Nelson or Castner-Kellner cell. Hydrogen and chlorine are the by-products of this industry.

The mechanism in the Nelson cell is represented below :

The solution contains Na^+ , Cl^- , and H^+ and OH^- (furnished by slight dissociation of water). At the cathode, H^+ ions will be discharged and **not** Na^+ ions as the discharge potential of Na^+ is very much higher. At the anode, Cl^- ions are discharged as the discharge potential of OH^- is comparatively higher. Thus,

At cathode :



At anode :



As H^+ and Cl^- ions are removed, there remain Na^+ and OH^- ions in solution. Therefore, on evaporating this solution, crystals of sodium hydroxide are obtained.

The mechanism of electrolysis of NaCl solution is represented in some books as :

At cathode :

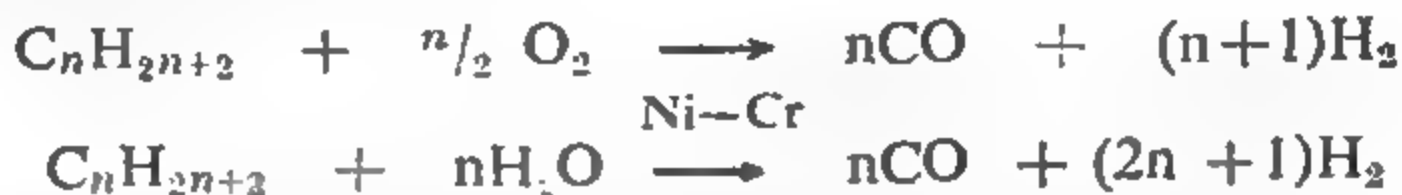


At anode :



This is incorrect because Na^+ ions cannot be discharged as long as H^+ ions are present in solution.

(v) **Recent Methods.** Recently new methods for industrial preparation of hydrogen have been devised. One of these methods is based on the partial oxidation of crude naphtha obtained from petroleum. The oxidation is brought about either by oxygen or by steam in the presence of nickel-chromium catalyst.

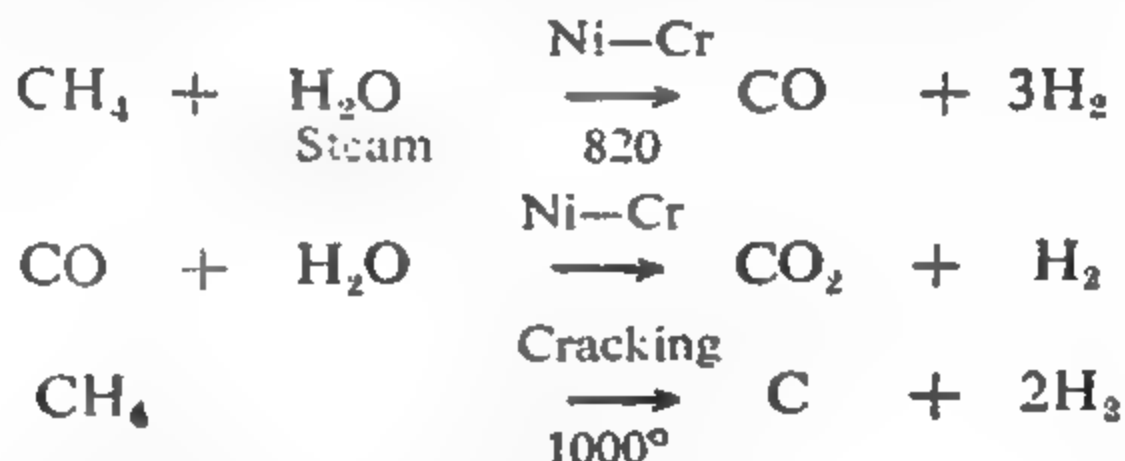


In the presence of excess of steam, some carbon dioxide may also be produced.



Hydrogen is separated from CO and CO_2 by the usual methods described above.

Another recent method involves partial oxidation or *cracking* of natural gas.



Hydrogen is separated in the usual way.

Physical Properties. Hydrogen is a colourless, tasteless and odourless gas. It is the lightest element known; the density with respect to air as 1 is 0.0695. It is sparingly soluble in water being less so than even oxygen. Its critical temperature is -236.9°C , at or below which it can be liquefied by the application of a suitable pressure. At -252.8° , it can be liquefied under a pressure of 1 atmosphere and at -259° , it can be solidified.

Chemical Properties. 1. **Combination with non-metals.** Hydrogen forms covalent compounds with a number of non-metallic elements, such as oxygen, nitrogen, fluorine, chlorine, bromine, etc. But at ordinary temperatures hydrogen is not so reactive. This is due to the fact that in molecular hydrogen, the atoms have the helium structure ($\text{H}:\text{H}$). It combines with oxygen, sulphur, nitrogen, bromine, iodine, etc., only when energy is supplied in the form of heat. With oxygen, for example, the reaction



is not perceptible even at 300° . The reaction is extremely slow even at 500° . It is only at 700° that the reaction becomes almost instantaneous.

At higher temperatures it becomes explosive. It is believed that when energy is supplied to the gaseous mixture in the form of heat, some of the molecules get dissociated into atoms which combine more readily. Further, as the reaction is exothermic, the heat produced dissociates more molecules into atoms and a cumulative effect is thus produced. This explains the instantaneous and explosive nature of the reaction.

When the combination of hydrogen and oxygen takes place in the presence of a catalyst, such as finely divided platinum or palladium, a similar explosive reaction results. It is believed that hydrogen molecules are first absorbed on the surface of the catalyst and are dissociated into atoms. The atoms then combine instantaneously with oxygen.

The combination with sulphur resulting in the formation of H_2S



also takes place at high temperatures.

The combination with nitrogen requires a high temperature ($450-500^\circ$) besides a high pressure (200 atmospheres) and the presence of a catalyst (finely divided iron) and molybdenum as a promoter, resulting in the formation of ammonia.



2. Combination with metals. Hydrogen combines with strongly electropositive metals, such as Li, Na, K, Ca, etc., to form hydrides.



The hydrides are *electrovalent* compounds (hydrogen forming an anion and behaving as an electronegative element), have high melting points and conduct electricity when fused. The metal hydrides find many industrial applications. Calcium and lithium hydrides for example, are used in portable hydrogen generators since they evolve a large amount of hydrogen when added to water. The hydrides are also good reducing agents.

3. Reducing properties. Hydrogen gas acts as a reducing agent. The oxides of the less electropositive metals, such as those of Cu, Zn, Pb, Fe, etc., are reduced when they are heated and hydrogen is passed over them.



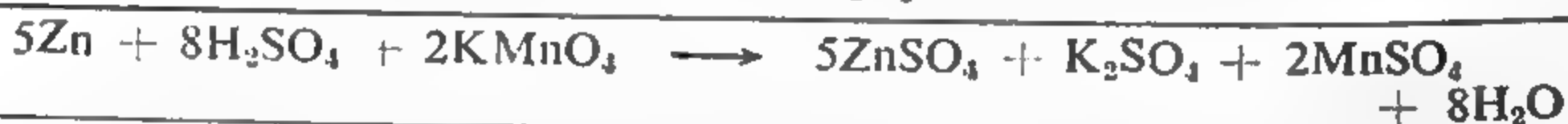
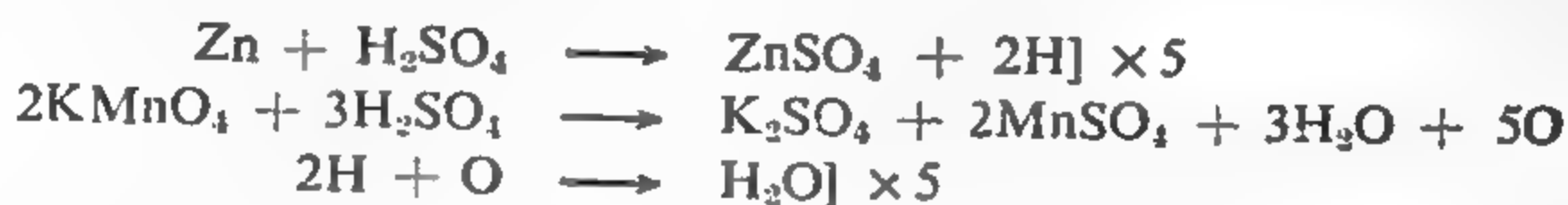
The oxides of strongly electropositive metals, such as those of alkali metals and alkaline earths, are not reduced by this method. Certain chlorides get reduced by hydrogen, e.g.,



Nasscent hydrogen. If hydrogen gas is passed through an acidified solution of potassium permanganate, the latter is not decolourised showing thereby that H_2 gas does not reduce potassium permanganate.

But if a piece of zinc is added to the solution, it is decolourised, *i.e.*, potassium permanganate is reduced. This shows that hydrogen at the moment of its formation is more active than the ordinary hydrogen gas. *The hydrogen produced in contact with the substance to be reduced is known as nascent hydrogen.*

According to one of the theories, hydrogen, at the moment of its liberation (by the action of zinc on sulphuric acid), is in the form of atoms which are extremely reactive on account of incomplete valency shells. These atoms react with the oxygen supplied by KMnO_4 and thereby the latter gets reduced.



In the ordinary hydrogen the atoms have already combined to form molecules (H_2) whereby the valency shells of both the hydrogen atoms get completed. The molecule, therefore becomes stable and comparatively inactive.

Hence, the nascent hydrogen is more active than ordinary (molecular) hydrogen.

Uses of Hydrogen. From the above discussion of physical and chemical properties it is easy to follow the important uses to which hydrogen has been put at various times.

1. **In balloons.** As hydrogen is the lightest gas known and its density is one fourteenth of that of air, it has been used since long in filling different types of balloons. But as the gas is inflammable, its use involves risk of fire. There have been several serious mishaps. In 1937, for example, the huge German balloon 'Hindenberg' caught fire while landing. Since that time balloons required for different purposes have been filled with the inert gas helium which, though heavier than hydrogen, is free from the risk of fire.

2. **Hydrogen generators.** The metallic hydrides, such as NaH and LiH are used in portable hydrogen generators, since, when put in water, they release a large amount of hydrogen. Tin and silicon hydrides have a high heat of combustion. They are being examined as rocket fuels.

3. **Hydrogenation processes.** Hydrogen gas is largely used in hydrogenation processes, that is, the processes in which hydrogen gas is added as such to compounds in the presence of a catalyst. A few examples are given below :

(i) Vegetable oils such as coconut oil, groundnut oil, cotton seed oil, which are liquid at ordinary temperatures, are treated with hydrogen at 170° in the presence of finely divided nickel. They take up hydrogen and change into semi-solid fats which are used as cooking medium in

several countries. The process is known as **hydrogenation** or 'hardening' of vegetable oils into edible fats such as margarine and 'vanaspati'.

(ii) Carbon monoxide takes up hydrogen, under pressure in the presence of a catalyst consisting of a mixture of zinc oxide and finely divided copper, to give methyl alcohol.



(iii) Hydrogen is used in the **petroleum industry** to extend the supply of gasoline.

(iv) Hydrogen is used in the production of **synthetic petroleum**. In the Bergius process, for example, the hydrogenation of coke is carried out at moderately high temperatures and extremely high pressures when several compounds of carbon and hydrogen which constitute different petroleum products such as gasoline, kerosene and lubricating oils, are produced.

4. **Oxy-hydrogen flame.** When hydrogen is burnt in oxygen, a very hot flame known as *oxy-hydrogen flame* with a temperature of about $2000-2500^\circ$ is produced. This temperature is sufficient to melt platinum and to cause a stick of lime to glow with a dazzling light known as *lime light*. It is used in welding and other allied purposes.

5. **Production of ammonia.** Appreciable quantities of hydrogen are being used at present in the production of ammonia by direct combination with nitrogen under pressure by Haber process. Ammonia is a valuable product as a refrigerant and as a source of fertilizers and explosives.

WATER

Water occurs widely in nature in liquid, solid and gaseous states. About 75 per cent of the earth's surface is covered by water. All living materials contain a very high proportion of this substance.

Until the close of the eighteenth century, water was believed to be a simple element. Cavendish showed (about 1781) that water is a compound of hydrogen and oxygen. Later, Lavoisier (1783) determined its composition by weight and assigned it the chemical formula H_2O .

Physical Properties At ordinary temperatures, pure water is a colourless, odourless and tasteless mobile liquid. It is transparent but appears bluish in thick layers.

Water freezes at 0°C into crystalline ice. The latent heat of fusion is 79.7 cal. per gram of ice.

Water boils at 100°C at an atmospheric pressure of 760 mm. to form steam. The *latent heat of vaporisation* is 539 cal. per gm. of water.

Water possesses a maximum density of 1 at 4° (more accurately at 3.98°); the density at 0° is 0.99878 .

Water, like other liquids, is very slightly compressible and 1000 c.c. of water subjected to a pressure of 2 atmospheres is reduced to 999.5 c.c.

It is a poor conductor of heat. The specific heat of water is taken as unity or in other words one calorie of heat is taken up by 1 gram of water at 14.5°C to raise its temperature by 1 degree.

Water possesses a high dielectric constant (81) and, therefore, salts get highly ionized when dissolved in it.

Water is a very poor conductor of electricity.

Chemical Properties. 1. **Thermal dissociation.** Water is a very stable compound and does not appreciably decompose even at high temperatures. It decomposes to the extent of 0.6% at 2040°C, while at 3500°C, about 3% is decomposed, the reaction being reversible.



2. **Electrolytic decomposition.** When an electric current is passed through water containing a little acid or alkali, it decomposes into hydrogen and oxygen, which are evolved respectively at the cathode and the anode.

3. **Action with metals.** Metals which lie above cobalt in the *electrochemical series* react with water and replace hydrogen from it. The more active metals like sodium, potassium, calcium, strontium, etc., react with water at *ordinary temperatures*.



Metals like magnesium and beryllium decompose only *hot water*.



The less active metals like iron, zinc, etc., decompose *steam* at red heat.



Metals like mercury, silver, gold and platinum have *no effect* on water.

4. **Action with non-metals.** Non-metals mostly do not react with water. Strongly electronegative halogens, *i.e.*, fluorine, and chlorine react with water at ordinary temperature. Fluorine forms hydrogen fluoride and ozonised oxygen, while chlorine forms hypochlorous and hydrochloric acids.



In the presence of light, chlorine evolves oxygen.

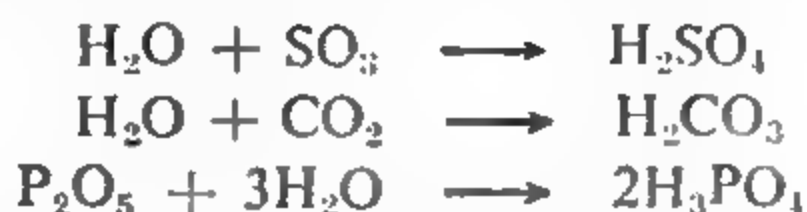


Carbon and silicon also decompose steam at red heat.

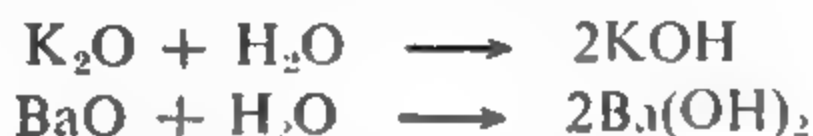


The reaction of silicon is rather slow.

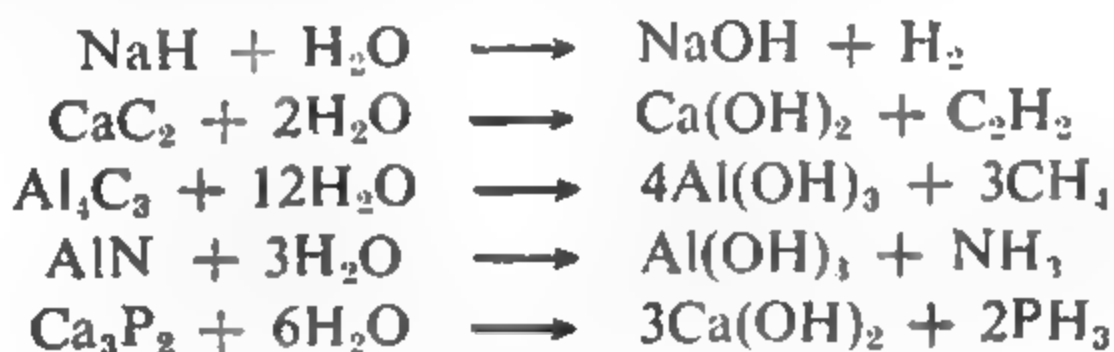
5. Reaction with oxides. Water combines with acidic oxides to produce oxy-acids, *e.g.*,



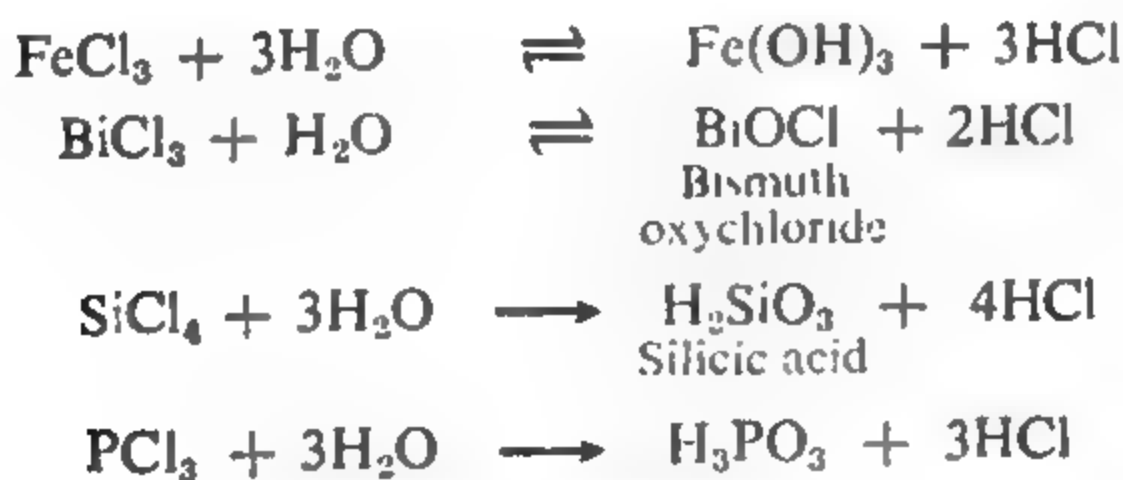
and with basic oxides to produce basic hydroxides or bases.



6. Reaction with metallic hydrides, carbides, nitrides, phosphides. Water reacts with metallic hydrides, carbides, nitrides and phosphides giving hydrogen, gaseous hydrocarbons, ammonia and phosphine, respectively.



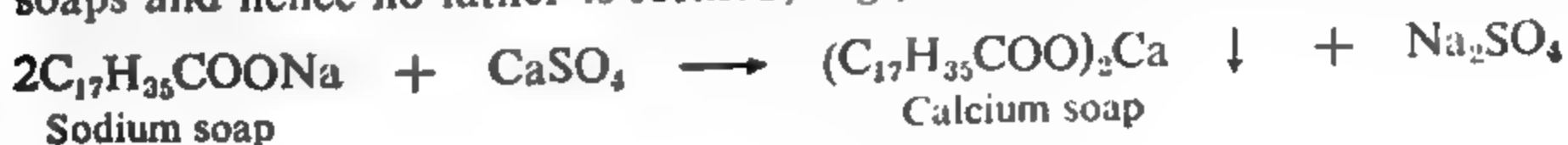
7. Reaction with chlorides of metals and non-metals.



Soft and Hard Water

Water from rivers, springs or even wells, contains a certain amount of dissolved mineral matters. Water containing soluble calcium and magnesium salts (principally bicarbonates, chlorides, and sulphates) is termed as hard water, and if these salts are absent, the water is called soft.

Hard water is not always harmful for drinking purposes but its use in the laundry work is wasteful as soap (which is a mixture of sodium salts of stearic, palmitic and oleic acids) reacts with any soluble calcium or magnesium salt giving precipitates of calcium or magnesium soaps and hence no lather is formed, *e.g.*,



Hard waters are also undesirable in dyeing, in rayon plants and in boilers.

Types of Hardness. Hardness of water is of two kinds :

(1) *Temporary hardness*, and (2) *Permanent hardness*.

Temporary Hardness. The hardness of water which can be removed by boiling is known as temporary hardness. It is due to the presence of bicarbonates of calcium and magnesium. When such a water is boiled, the bicarbonates decompose forming the insoluble carbonates.



Permanent Hardness. The hardness of water which cannot be removed by boiling is known as permanent hardness. It is due to the presence of sulphates and chlorides of calcium and magnesium which do not decompose on heating.

Softening of Water. The process of removing the calcium and magnesium salts from hard water is called *softening* the water. Temporary hardness may be removed simply by boiling, when the soluble bicarbonates get converted into the insoluble carbonates and thus get separated. Temporary hardness may also be removed by the **Clarke's lime process** which consists in adding a calculated amount of lime. The calcium and magnesium carbonates are formed which are separated by filtration.



Permanent hardness may be removed by heating water with sodium carbonate or borax, in which case calcium carbonate or calcium borate is precipitated.



The methods of softening of water described above are rather too expensive and inconvenient for application on a large scale. The following modern methods are replacing them rapidly.

(1) **Permutit process.** Permutit is a trade name given to the artificially made sodium aluminium ortho-silicate which is allied to the natural mineral, *zeolite*, $\text{NaAlSiO}_4 \cdot x\text{H}_2\text{O}$. The use of permutit as a water softener is based on its property of exchanging its sodium for calcium and magnesium, which it does when brought in contact with solutions containing these cations. If we use, for permutit, the abbreviated formula NaZ , then the exchange between the cations would take place according to the following equations :



The permutit is packed in a cylinder and the hard water is made to percolate slowly through it (Fig. 10.2). The Na^+ ions of the permutit replace Ca^{++} and Mg^{++} ions in the water, and the softened water is drawn from the bottom of the cylinder. After use for a period of time, the permutit gets exhausted (in as much as all the Na^+ ions get exchanged by Ca^{++} or Mg^{++} ions). The exhausted permutit is revived by passing a 10% solution of sodium chloride through it when the Na^+ ions from NaCl replace the Ca^{++} and Mg^{++} ions in the permutit.



The revived permutit is again used and this process can be repeated a number of times, the consumption being only of common salt (NaCl) which is quite inexpensive.

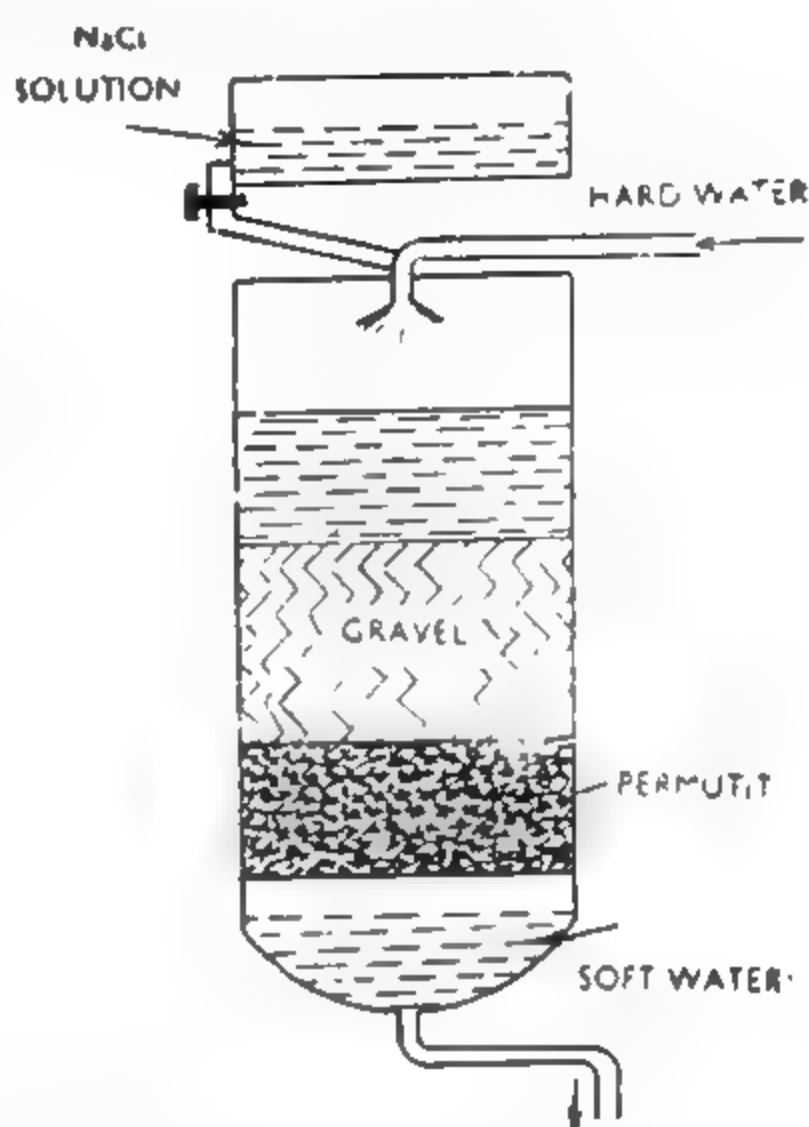


Fig 10.2. Permutit process for water softening.

(2) **Demineralization of water with ion exchange resins.** Recently, synthetic resins (high polymers) of the bakelite type, such as the one made from sulphonated phenol and formaldehyde, are finding increasing applications as **ion exchangers**. The various salts present in water can be removed by passing it through a cation exchange resin (H_2R) which replaces all cations in the water with the hydrogen ions.



The water which now contains H^+ ions is passed through an anion exchange resin $\text{R}(\text{OH})_2$. This exchanges the anions present in water for the OH^- ions, which in turn form water with the H^+ ions.

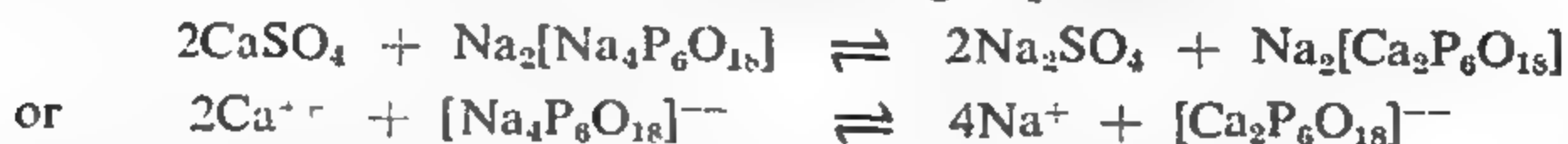


Thus, water is completely free from all mineral matter and this process is called **demineralization**. This water is almost as free of dissolved salts as distilled water.

The two kinds of resins used above are regenerated at periodic intervals by treatment with sulphuric acid and sodium carbonate solution respectively.

(3) **Calgon method.** Sodium hexa metaphosphate $(\text{NaPO}_3)_6$ is a new product now used as a water softener. This compound is commercially known as *calgon* meaning "calcium gone". Calgon is a complex compound having four atoms of sodium inside the complex anion and has the formula $\text{Na}_2[\text{Na}_4\text{P}_6\text{O}_{18}]$. It reacts with calcium ions forming a

soluble complex salt containing calcium inside the complex anion. The reaction may be represented by the following equation :



Since the calcium gets tied up in the anion, it does not give any precipitate with soap and hence the hard water after the addition of calgon, forms lather easily with soap or in other words gets softened. Further, since calgon takes up Ca^{++} ions from solution, it will dissolve calcium compounds which are insoluble in water and which comes down as scales and incrustations in a boiler. Calgon has, therefore, found wide use in softening hard waters and in the removal of calcareous deposits in boilers.

Water for Industrial Purposes. Water is chiefly used in industries for steam making. Natural water containing dissolved and suspended impurities when used in boilers causes the following two principal difficulties :

- (i) Formation of scale (ii) Corrosion.

Formation of scale. Formation of scale is the deposition of mineral matter within the boiler shell and the deposit is called *incrustation* if hard and *sediment* or *sludge* if soft and bulky. The scale of incrustation consists of silica, iron and aluminium oxides, calcium carbonate and sulphate and magnesium oxide and carbonate. If magnesium and sulphate contents are low, the scale is soft and bulky and may be in the form of *sludge*.

The boiler scale is a poor conductor of heat and so causes a waste of fuel. The sludge can be blown or washed away from the boiler but the hard scale of incrustation is difficult to get rid off. Besides increasing the fuel consumption, the incrustation increases also the cost of boiler repair. As the crust prevents the ready transfer of heat to the water in the boiler, the iron in contact with the flames is often heated to redness. Due to uneven cracking of the crust, the water suddenly comes into contact with the red hot iron. Consequently sudden formation of steam and release of hydrogen may result in a serious explosion.



Corrosion. Corrosion or "pitting" is caused chiefly by the solvent action of acids on the iron of the boiler. Acids produced by the hydrolysis of iron, aluminium and magnesium salts are the chief cause of corrosion.



Besides, dissolved oxygen and free carbon dioxide also bring about corrosion. Certain natural waters contain free hydrogen sulphide, sulphuric acid, etc. Such waters if used in boilers, would readily bring about corrosion. The slow but constant corrosion of the boiler causes it to leak, particularly, around the rivets, and damages the boiler seriously.

Composition of Water.

(A) By Weight. 1. Morley's method. Morley determined the composition of water (by weight) by burning weighed quantities of hydrogen and oxygen and weighing the water formed. The apparatus used is shown in Fig. 10.3,

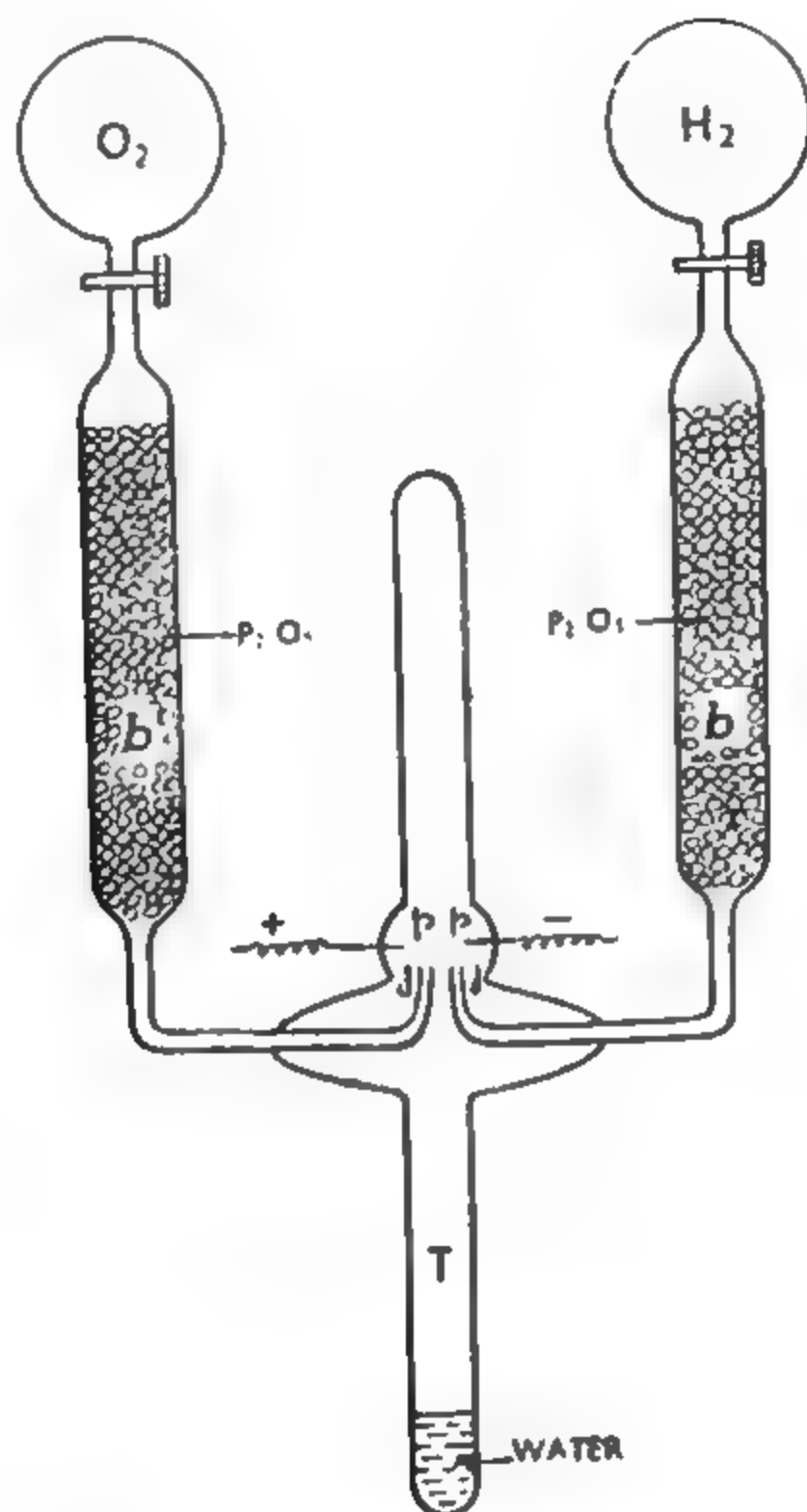


Fig. 10.3. Morley's method for determination of composition of water by weight.

Pure and thoroughly dried hydrogen and oxygen were taken in large glass globes and weighed. The globes were then connected to the main apparatus which was previously exhausted. The gases passed through the P_2O_5 tubes b, b to the jets j, j where they were ignited by passing an electric spark between the platinum wires p, p . The lower part of the apparatus was cooled in water so that the water vapour formed as a result of the ignition of the gases, immediately condensed and trickled down into the lower tube T . This water was frozen and the residual gases consisting of unburnt hydrogen and oxygen were pumped off through the P_2O_5 tubes back to the globes and analysed. From this, the weight of oxygen and hydrogen which had combined to form water could be evaluated. Knowing the weight of water formed, the composition of water could be easily calculated.

As a result of twelve experiments, Morley determined that oxygen and hydrogen are present in water in the ratio of 8 : 1.00762.

2. Dumas' Method. In this method, *dry* hydrogen gas was passed over heated copper oxide taken in a weighed tube when hydrogen was oxidised to water and copper oxide reduced to copper.



The water formed was absorbed in weighed calcium chloride tubes. The loss in the weight of the copper oxide tube gave the weight of the oxygen which had combined with hydrogen to form water. Knowing the weight of water, weight of oxygen and of hydrogen (by difference), the composition of water could be calculated. The data gave the ratio of hydrogen to oxygen as 1 : 7.98.

B. By Volume. (1) By synthesis. The composition of water by volume can be determined by exploding a mixture of hydrogen and oxygen over mercury in a eudiometer tube. In one experiment, 25 c.c. of hydrogen were exploded with 10 c.c. of oxygen. The water formed condensed on cooling and occupied negligible volume. The residual hydrogen was found to occupy a volume equal to 5 c.c. (cf. Fig. 10.4).

Thus, 20 c.c. of hydrogen combined with 10 c.c. of oxygen to form water. In other words, the ratio of hydrogen to oxygen in water is 2 : 1 by volume.

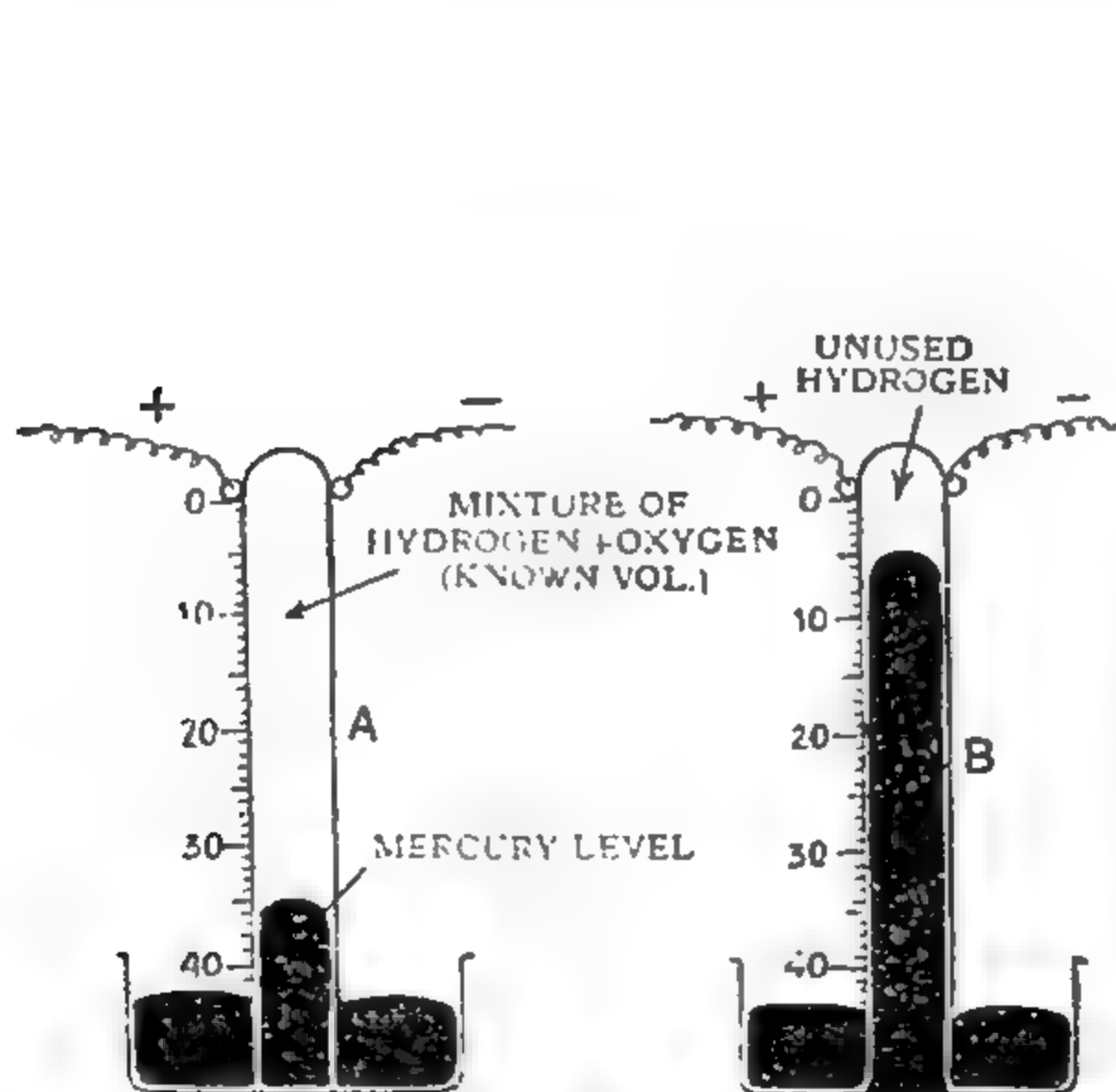


Fig. 10.4. Composition of Water (by synthesis).

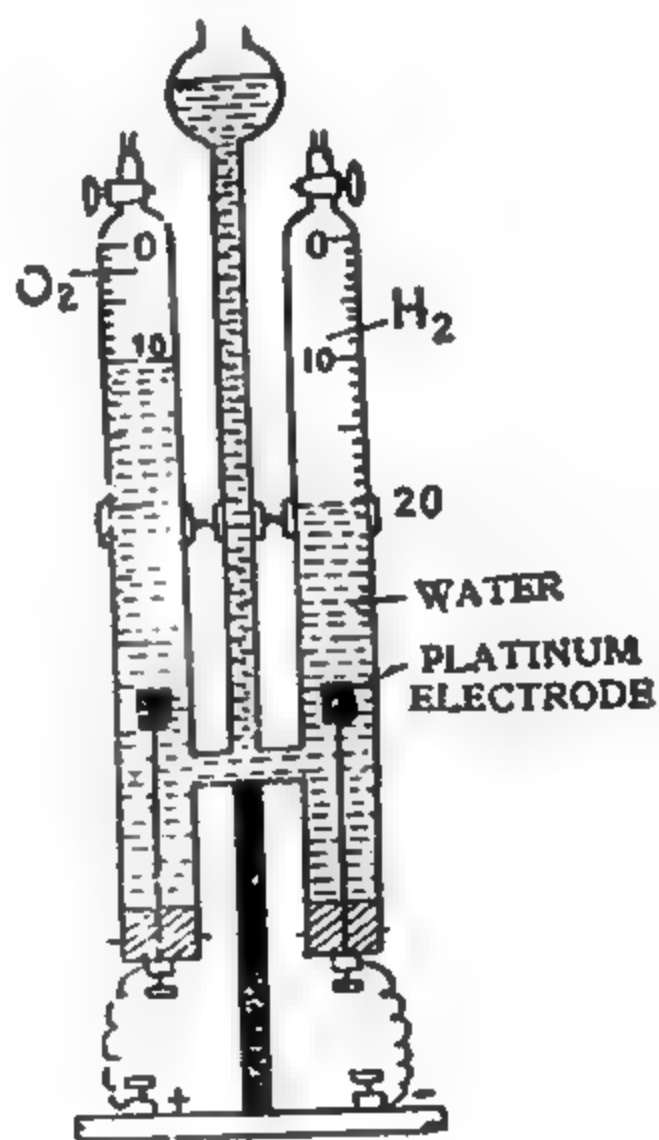


Fig. 10.5. Composition of Water (by analysis)

2. By analysis. The composition of water by volume was also determined by electrolysis of acidulated water in a voltameter (Fig. 10.5), when the volume of hydrogen evolved was double the volume of oxygen evolved, indicating thereby that the ratio of hydrogen to oxygen is 2 : 1.

QUESTIONS

1. Describe how hydrogen may be obtained from (i) water (ii) acids (iii) alkalies. Discuss its important uses.
2. How is pure hydrogen obtained? Describe the important properties of the gas.
3. How is hydrogen prepared on an industrial scale? Describe its important industrial uses.
4. Describe the action of water on the following :
 (1) Sodium hydride (2) Calcium carbide (3) Aluminium phosphide (4) Aluminium nitride (5) Calcium phosphide (6) Phosphorus trichloride (7) Phosphorus pentoxide (8) sulphur trioxide.
5. What is meant by hardness of water? Differentiate between temporary and permanent hardness of water. How is temporary hardness removed?
6. What is meant by temporary and permanent hardness of water. What is it due to? Explain Permutit process for the removal of hardness.
7. What are the causes of hardness of water? Why is hard water unfit to be used in boilers?
8. How is the composition of water determined (i) by weight (ii) by volume.

CHAPTER XI

OXIDES OF NITROGEN

Nitrogen forms a number of oxides, five of which have been positively known and studied. The formulae, names and physical appearance of these oxides are given in Table 11.1.

TABLE 11.1
Oxides of Nitrogen

Formula	Name	Physical appearance
N_2O	Nitrous oxide	Colourless gas
NO	Nitric oxide	Colourless in the gaseous state (blue in the liquid and solid states)
N_2O_3	Dinitrogen trioxide	Blue solid
NO_2 \Downarrow N_2O_4	Nitrogen dioxide \Downarrow Dinitrogen tetroxide	Brown gas Colourless gas
N_2O_5	Dinitrogen pentoxide	Colourless gas

Two more oxides NO_3 and N_3O_6 have also been reported. There is some spectroscopic and chemical evidence in favour of their existence. The oxide NO_3 is reported to be produced by the action of ozone with N_2O_5 , while the oxide N_3O_6 has been shown to be formed by the action of fluorine on nitric acid. But they have not been isolated.

Nitrous Oxide

Preparation. Nitrous oxide is prepared in the laboratory as well as on a commercial scale by carefully heating ammonium nitrate up to 240° .



The gas may be contaminated with nitric oxide (NO) which is removed by passing through ferrous sulphate solution. Water can be easily removed with cold trap.

In the laboratory, the gas is collected over *hot* water (as the gas is fairly soluble in cold water) and on a commercial scale it is stored in steel cylinders under a pressure of about 100 atmospheres.

Physical Properties. Nitrous oxide is a colourless gas fairly soluble in cold water but practically insoluble in hot water. It can be easily liquefied at room temperatures by applying pressure as its critical temperature is 35° . It has a faint odour. When inhaled in moderate quantities, it produces hysterical laughter, hence, the name, *laughing gas*. In small amounts, it acts as an anaesthetic.

Chemical Properties. Chemically nitrous oxide is relatively inert. It does not react with halogens, alkali metals and ozone at room temperatures. At high temperatures, it decomposes into nitrogen and oxygen and reacts with alkali metals to form oxides and supports combustion.

Uses. Commercially, it is used as the propellant gas in 'whipped' cream bombs. It is also used as an anaesthetic.

Composition of Nitrous Oxide. The composition of nitrous oxide may be established with the help of the apparatus shown in Fig. 11.1. It consists of two glass tubes (one of which is graduated), connected together by means of a rubber tubing. The tubes are partly filled with mercury. The graduated tube is fitted with a cork through which two delivery tubes and two copper wires are passing. The delivery tubes carry stop cocks. One copper wire holds a spoon and the other carries a platinum wire at the lower ends (see Fig. 11.1).

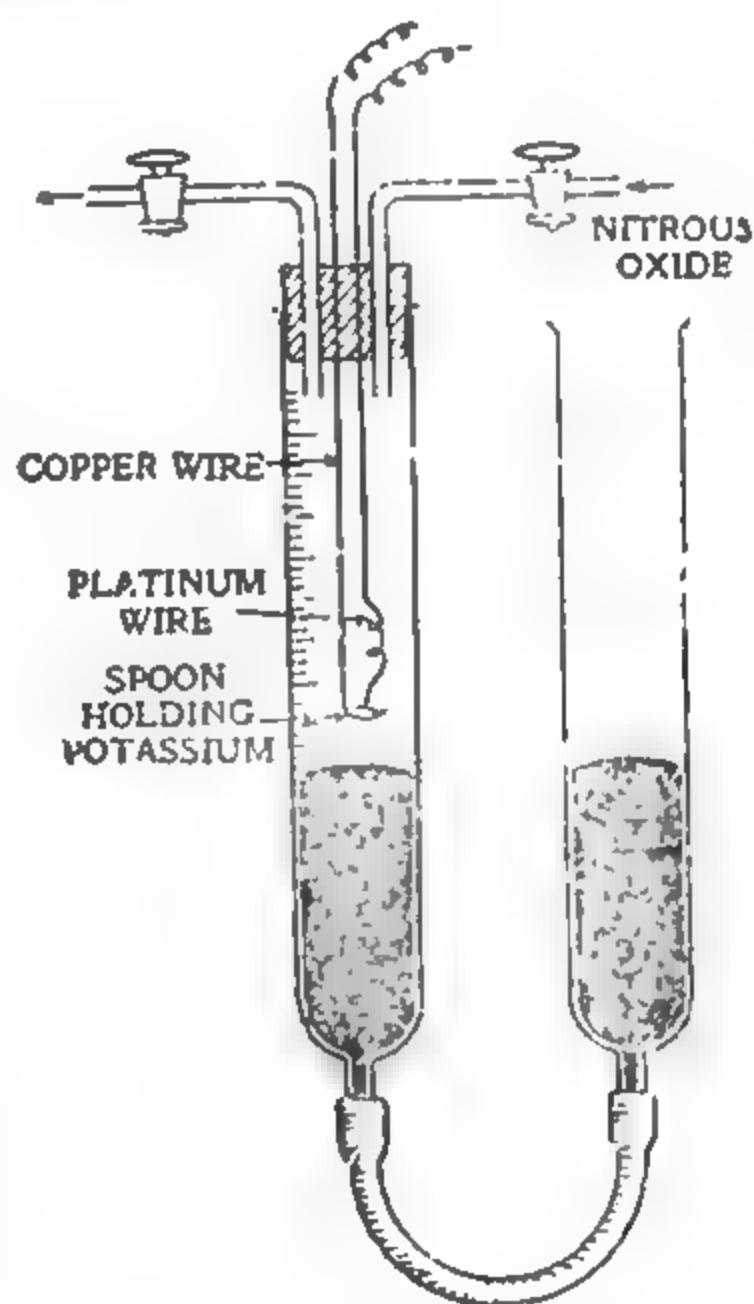


Fig. 11.1. Composition of nitrous oxide.

A small piece of potassium is placed in the spoon and the graduated tube is filled with nitrous oxide. The level of mercury in both the glass tubes is made the same. An electric current is passed through the copper wires. A spark is passed between the spoon and the platinum wire as a result of which the potassium catches fire. It burns in nitrous oxide leaving behind nitrogen in the glass tube. When cooled to room temperature, the mercury is seen to stand at the same level indicating no change in volume.

This shows that one volume of nitrous oxide on decomposition gives one volume of nitrogen.

By Avogadro's law, one molecule of nitrous oxide on decomposition gives one molecule (or two atoms) of nitrogen.

Hence, the formula of nitrous oxide may be written as N_2O_x . Its molecular weight will, therefore, be $28 + 16x$.

The vapour density of the gas was found to be 22, so that its molecular weight is 44.

$$\text{Thus,} \quad 28 + 16x = 44$$

$$\therefore \quad x = 1$$

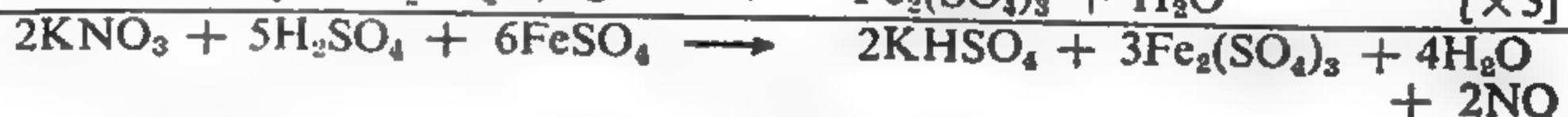
\therefore Molecular formula of nitrous oxide is N_2O .

Nitric Oxide, NO

Preparation. (1) In the laboratory, nitric oxide is usually prepared by the action of cold dilute nitric acid on copper turnings.



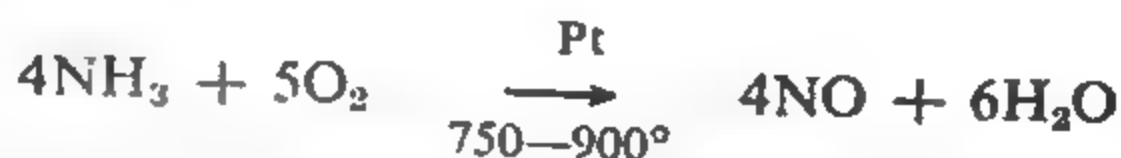
(2) A reasonably *pure* sample of nitric oxide may be prepared in the laboratory by the reduction of nitric acid with ferrous sulphate. For this purpose, a mixture of ferrous sulphate and potassium nitrate (in the ratio of 4 : 1) is placed in a conical flask and a small amount of water added to it. The flask is provided with a dropping funnel and a delivery tube. Concentrated sulphuric acid is added gently from the dropping funnel and the flask is *heated*. A steady stream of nitric oxide is evolved. The various reactions may be represented as :



(3) Instead of potassium nitrate, nitrite of sodium or potassium may also be used, when nitric oxide is evolved without any heating. The overall reaction is



(4) On a commercial scale, nitric oxide is obtained by the catalytic oxidation of ammonia.



(5) Nitric oxide may also be obtained by the direct combination of nitrogen and oxygen of the air at a high temperature (3000°) :



The yield of nitric oxide, however, is very low. Hence the reaction has not been developed as a practical industrial synthesis.

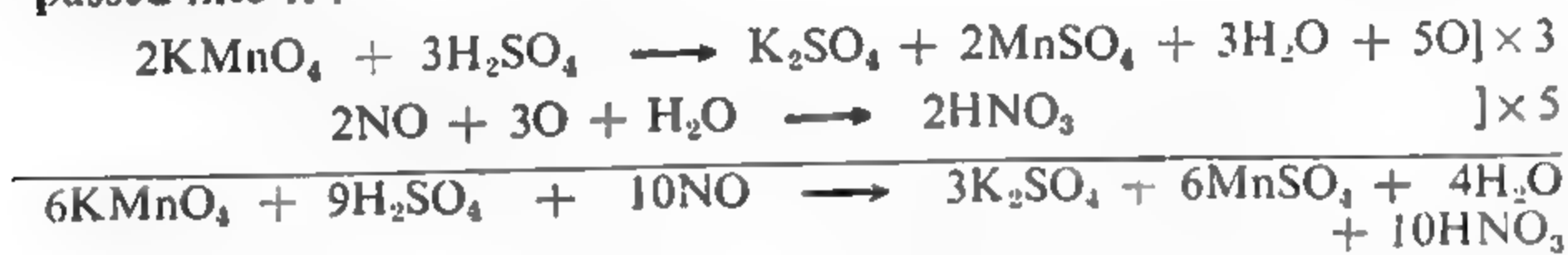
Physical Properties. Nitric oxide is a colourless gas which readily combines with atmospheric oxygen giving brown nitrogen dioxide. Hence, the gas must be handled out of contact with air. Since its critical temperature is very low (-93°) it can be liquefied only with some difficulty. The liquid has a blue colour which boils at -142.8° and freezes at -150° . It is neutral in character.

Chemical Properties. The most important reactions of nitric oxide are those of oxidation and reduction.

(1) It readily combines with oxygen giving brown nitrogen dioxide.



(2) It is easily oxidised to nitric acid by strong oxidising agents such as potassium permanganate, dichromate, halogens, etc. Thus, acidified potassium permanganate is decolourised when nitric oxide is passed into it :



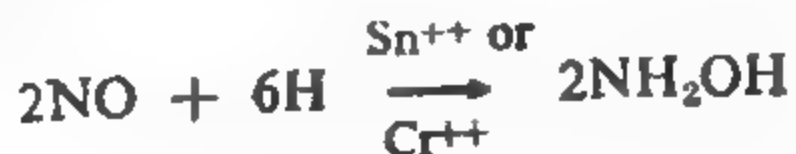
The reaction with KMnO_4 is quantitative and is used for the estimation of nitric oxide.

(3) Nitric oxide is oxidised to nitrogen dioxide with conc. nitric acid.

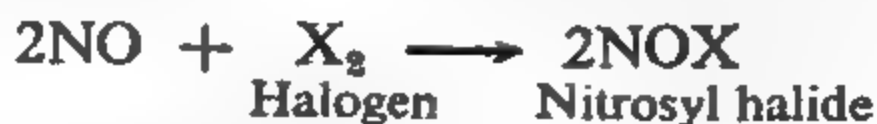


This reaction is of particular interest because it explains why metals like copper, silver, mercury, etc., give *nitric oxide* with *dilute* nitric acid but *nitrogen dioxide* with concentrated nitric acid. In the case of dilute nitric acid, that is, when sufficient water is present, the reaction is pushed backwards giving nitric oxide, but with concentrated nitric acid, the reaction proceeds in the forward direction giving nitrogen dioxide. It follows from this that at some intermediate concentration of nitric acid, both NO and NO_2 should be formed. It is actually so. A 5*N* solution of nitric acid gives an almost equimolecular mixture of NO and NO_2 on reaction with copper.

(4) Nitric oxide is reduced also equally easily. With sulphurous acid it is reduced to nitrous oxide while with chromous or stannous ions, it yields hydroxyl amine.



(5) Nitric oxide directly combines with halogens (fluorine, chlorine, bromine but not iodine) to give the corresponding nitrosyl halides.



These halides are highly reactive and are used as powerful oxidising agents.

(6) Nitric oxide is absorbed in ferrous sulphate solution giving a dark-brown colouration (*a test for nitric oxide and nitrates*). The brown colour is due to the formation of a hydrated nitrosyl complex of iron, having the formula $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{++}$. This compound is responsible for the brown ring in the test for nitrates.

This complex is stable only at low temperatures. On heating, it decomposes to set free nitric oxide. The reaction, therefore, provides a method for the purification of the gas as well as for its separation from other gases.

Composition of Nitric Oxide. The composition of nitric oxide may

be determined with the help of the apparatus shown in Fig. 11.2. It consists of a long graduated tube connected to mercury reservoir with the help of a rubber tube. The glass tube is fitted with a cork through which a delivery tube and a loop of iron wire are passing as shown.

The mercury reservoir is raised upwards to raise the level of mercury in the glass tube up to the cork. This is done to eliminate the air present in the glass tube. The source of nitric oxide gas is then connected to the glass tube through the delivery tube and the mercury reservoir is lowered. Nitric oxide fills the glass tube. The level of mercury in both the limbs is made the same and the stop cock of the delivery tube closed. The volume of nitric oxide admitted into the glass is noted.

The iron wire is then strongly heated by passing an electric current. Nitric oxide reacts with iron giving iron oxide and liberating nitrogen. After cooling to room temperature, the level of mercury is once again made the same in both the limbs and the volume of nitrogen is noted.

The volume of nitrogen is found to be one half of the volume of nitric oxide taken. This shows that one volume of nitric oxide gives one half volume of nitrogen. Applying Avogadro's law, one molecule of nitric oxide contains one half molecule (or one atom) of nitrogen.

The formula of nitric oxide may, therefore, be written as NO_x . Its molecular weight will be $14 + 16x$.

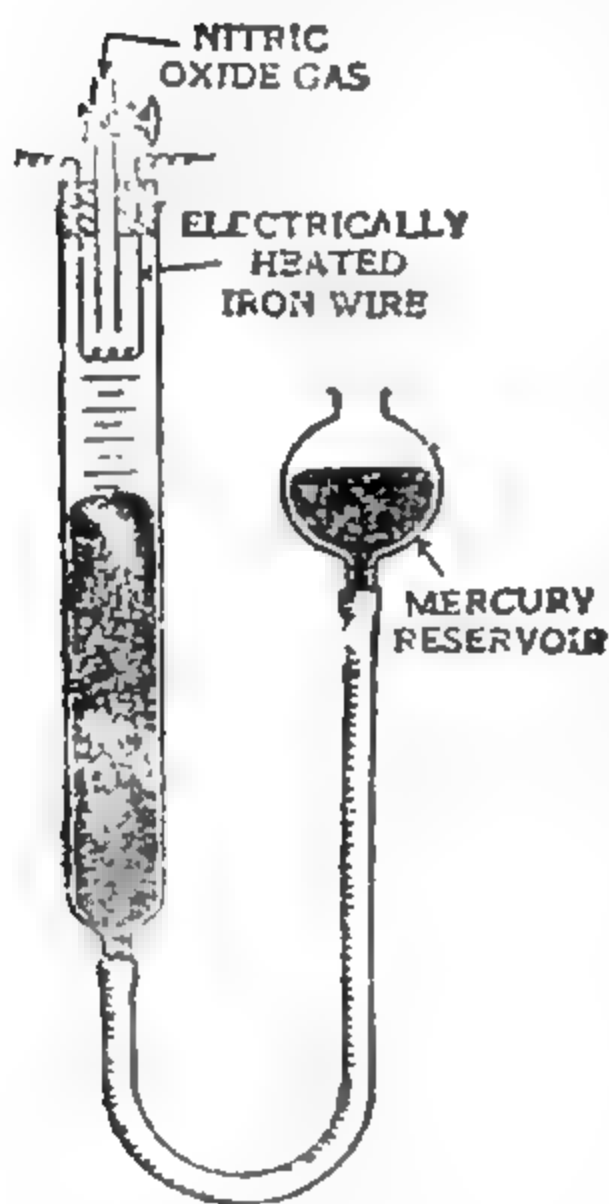


FIG. 11.2 Composition of nitric oxide.

The vapour density of nitric oxide has been found to be 15, so that its molecular weight is 30.

$$14 + 16x = 30$$

$$x = 1$$

Hence, the molecular formula of nitric oxide is NO.

Dinitrogen Trioxide, N_2O_3 .

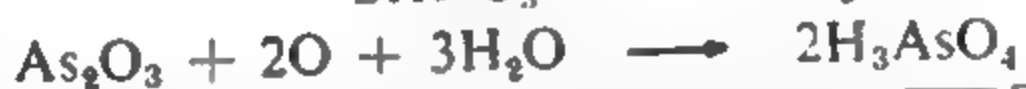
The oxide, N_2O_3 , exists pure only in the *solid state* at very low temperatures. Even in the liquid state it is dissociated into NO and NO_2 .



In the vapour state, it is almost entirely present as an equimolecular mixture of NO and NO_2 .



Such a mixture can be conveniently prepared in the laboratory by the reduction of 50 per cent nitric acid with arsenious oxide or of 5N nitric acid with metallic copper.



The brown mixture of NO and NO_2 when cooled in a freezing mixture, condenses to give a blue liquid which freezes to a blue solid.

The oxide, N_2O_3 , is formally referred to as the *anhydride of nitrous acid*. An equimolecular mixture of NO and NO_2 when dissolved in alkalis produces practically *pure* nitrites.



Nitrogen Dioxide, NO_2 and Dinitrogen Tetroxide, N_2O_4 .

These two oxides are in a temperature-dependent equilibrium :



In the solid state, the oxide consists only of N_2O_4 molecules and is colourless. At -11.2° , the solid melts. Even in the liquid state, partial dissociation occurs and the liquid may be considered as a dilute solution of NO_2 in N_2O_4 . The colour of the liquid gradually changes from yellow to orange with the rise in temperature indicating an increase in the percentage of NO_2 . At 22° , the liquid boils giving brown vapours. At 100° , the composition of the mixture has been found to be 90 per cent NO_2 and 10 per cent N_2O_4 . Above 140° , the dissociation is complete and the oxide consists only of NO_2 molecules. Beyond this temperature, the nitrogen dioxide starts dissociating into nitric oxide and oxygen, both of which are colourless :



Above 620° , the gas becomes colourless indicating a complete dissociation into NO and O_2 . All these changes are reversed on cooling. At some intermediate temperature (found to be 300° experimentally), the equilibrium mixture contains equimolecular quantities of NO_2 and NO. Thus, if the gas at 300° is treated with alkalis, it produces pure nitrite.



This fact is utilised in the commercial preparation of sodium nitrite.

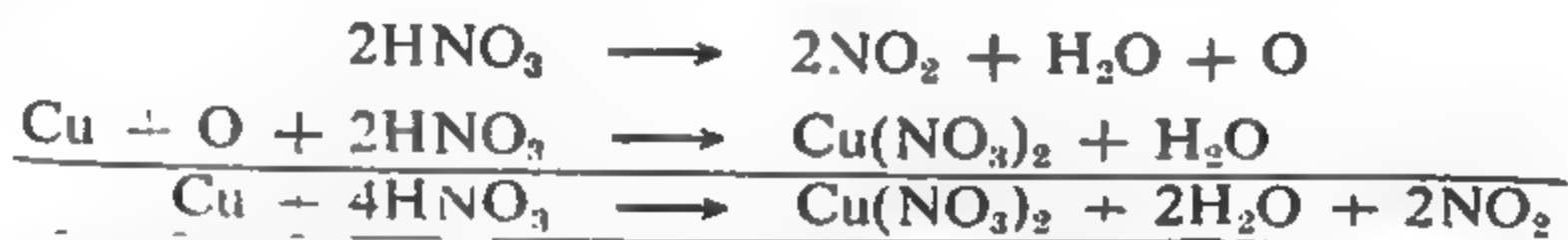
Preparation. The mixed oxides can be prepared by the following methods :

(i) *By heating nitrates of heavy metals.* Lead nitrate is most suitable as it is available in anhydrous condition and gives dry NO_2 .



Nitrogen dioxide is separated from oxygen by passing through a U-tube immersed in a freezing mixture when NO_2 condenses to an orange liquid while oxygen escapes.

(ii) *By the reduction of nitric acid with metals.* Concentrated nitric acid is readily reduced by metals like copper, silver, lead, etc., giving nitrogen dioxide.



(iii) *By the oxidation of nitric oxide.* Nitric oxide is readily oxidised to nitrogen dioxide when exposed to atmospheric oxygen.



Properties. As already mentioned, the oxide N_2O_4 is colourless while NO_2 is brown and the two oxides are in a temperature-dependent equilibrium :



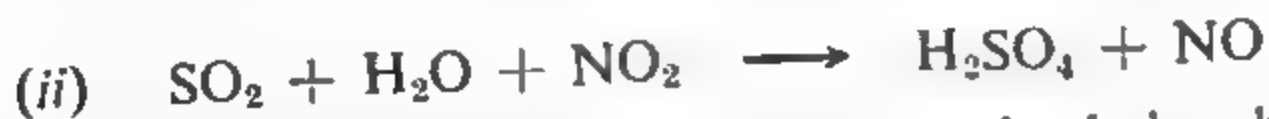
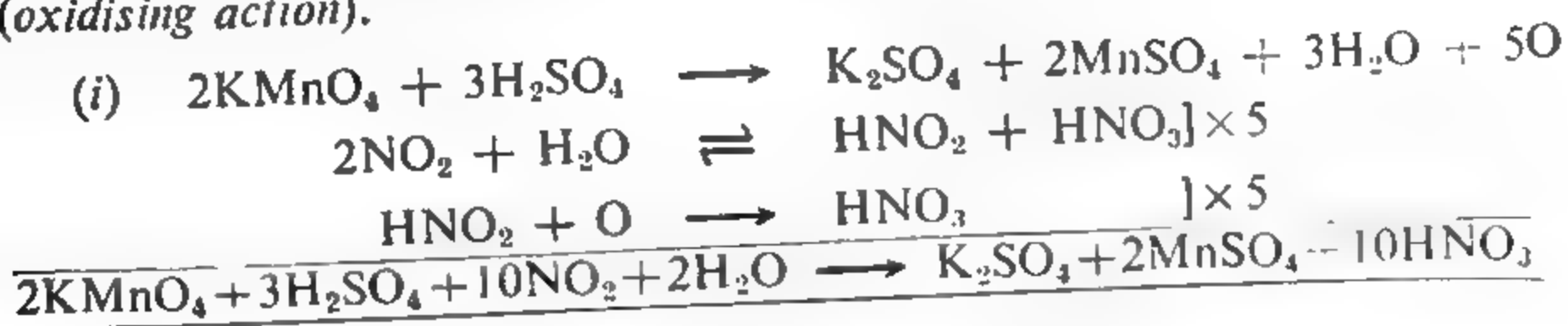
Nitrogen dioxide, when dissolved in water, gives a mixture of nitrous acid and nitric acid.



Hence, it is formally known as the "mixed anhydride" of these two acids.

In aqueous solution, nitrogen dioxide gives the reactions of both HNO_2 and HNO_3 . Like nitrous acid, it behaves as a reducing agent and like nitric acid it exhibits oxidising properties. Thus, nitrogen dioxide readily decolourises potassium permanganate (*reducing action*) and

converts sulphur dioxide to sulphuric acid in the presence of water (oxidising action).



The manufacture of sulphuric acid by lead chamber process is based on the oxidation of sulphur dioxide by nitrogen dioxide in the presence of steam.

Dinitrogen Pentoxide, N_2O_5 .

It is prepared by the dehydration of nitric acid with P_4O_{10} .



A mixture of concentrated nitric acid and phosphorus pentoxide is distilled in an all-glass apparatus in the presence of ozonised oxygen. The latter is essential to avoid the decomposition of N_2O_5 .

Properties. Dinitrogen pentoxide forms colourless crystals below 0° . As the temperature rises, the colour changes to yellow on account of the partial decomposition of N_2O_5 to brown NO_2 .



The crystals melt at 30° giving a yellow liquid which decomposes at 40° to give brown NO_2 .

It is highly deliquescent and readily dissolves in water with a hissing noise giving nitric acid.



Thus, the oxide is also referred to as nitric anhydride.

It acts as a strong oxidising agent.

QUESTIONS

1. What are the important oxides of nitrogen? Give their formulae, names and physical appearance.
2. How is nitrous oxide prepared in the laboratory? How is the composition of the gas established?
3. Describe the methods for the preparation of nitric oxide. Discuss its important properties. How is the composition of the gas determined?
4. How is nitrogen trioxide prepared? Why is it called the anhydride of nitrous acid?
5. Describe the various methods for the preparation of nitrogen dioxide. Show that it behaves both as an oxidising and a reducing agent.
6. What are the important oxides of nitrogen? Describe two of them in details.
7. Name the five oxides of nitrogen. How will you prepare each one of them from nitric acid.

(Jammu & Kashmir T.D.C. (I) 1967)

CHAPTER XII

PHOSPHORUS HALIDES AND PHOSPHORIC ACIDS

Phosphorus combines directly with halogens forming trihalides and pentahalides. Out of these, the trichloride and the pentachloride are the most important.

Phosphorus Trichloride, PCl_3

Preparation. Phosphorus trichloride is prepared by heating white phosphorus in a current of dry chlorine.



The apparatus is shown in Fig. 12.1. Dry, white phosphorus is placed in the retort and gently heated on a water bath. A current of pure, dry chlorine is led over the phosphorus. The phosphorus trichloride formed being volatile (b. p. 74°) distils over and is collected in a water cooled receiver.

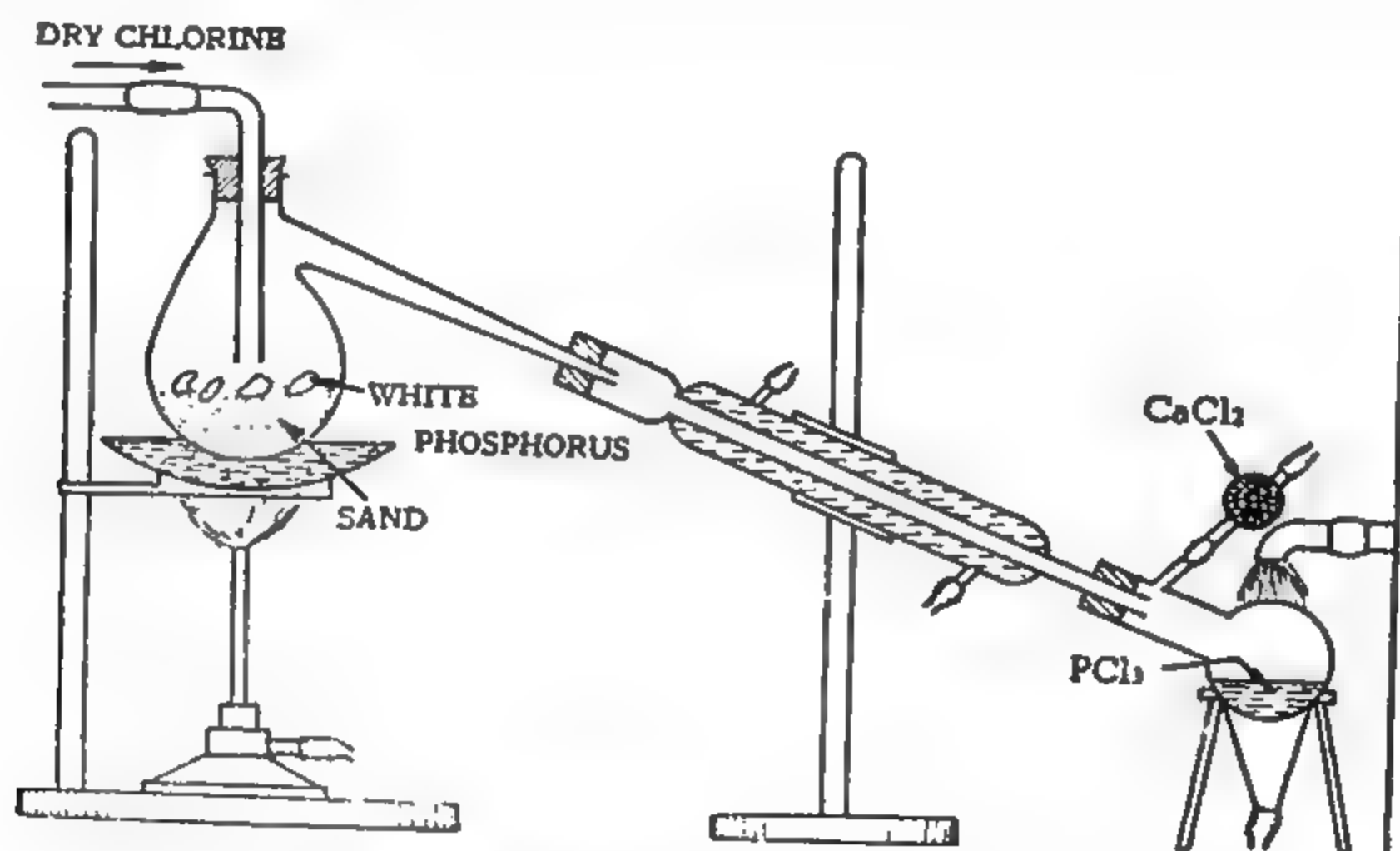
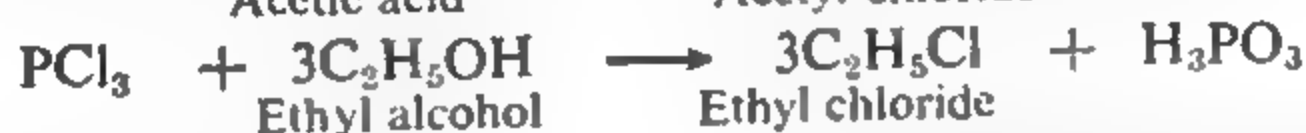
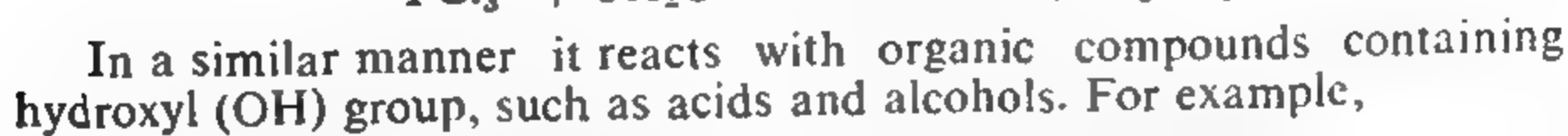
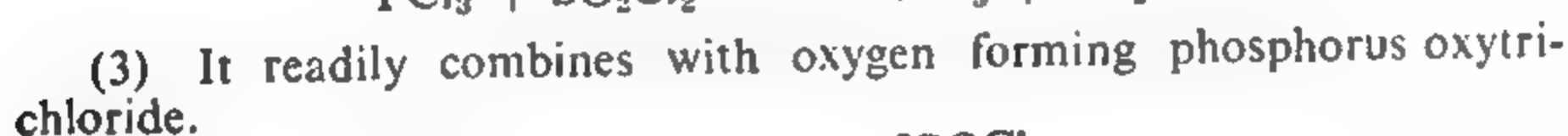


Fig. 12.1. Laboratory preparation of phosphorus trichloride.

The phosphorus trichloride obtained above contains some phosphorus pentachloride as impurity. The latter is removed by distilling the phosphorus trichloride over white phosphorus.

*Vapour density of phosphorus corresponds to the formula P_4 .

Chemical Properties. (1) It is violently hydrolysed by water giving phosphorous acid and hydrochloric acid gas.


$$\text{PCl}_3 + \text{Cl}_2 \longrightarrow \text{PCl}_5$$


Preparation. Phosphorus pentachloride is usually prepared by the action of an excess of chlorine on phosphorus trichloride.



Phosphorus trichloride is allowed to drop slowly and at the same time a current of dry chlorine is passed through the bottle. When the required amount of phosphorus pentachloride has been obtained, the excess of chlorine is removed from the bottle by flushing with carbon dioxide. The bottle is then carked.

Physical Properties. Phosphorus pentachloride is a yellowish white crystalline compound having a sharp odour. It sublimes on heating at 160° and melts at 45° under pressure.

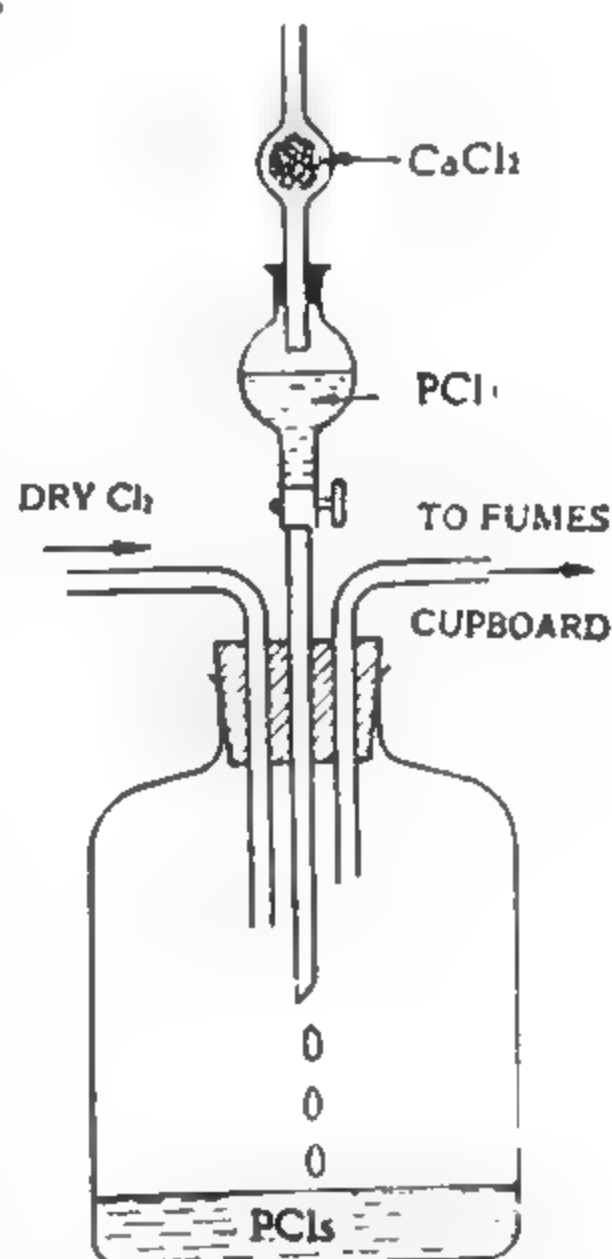
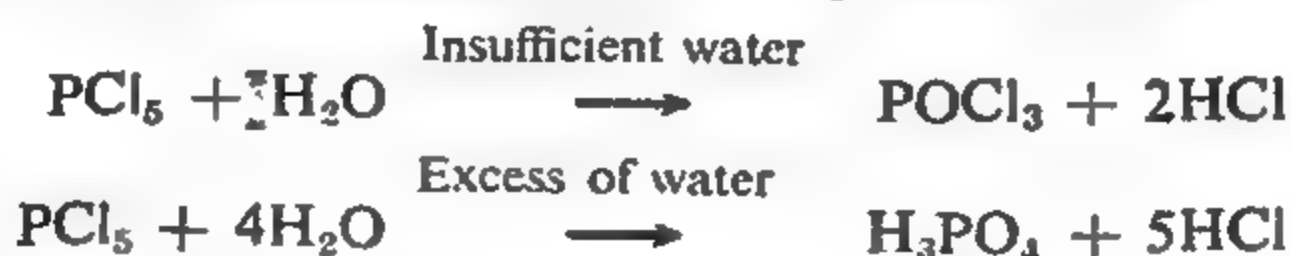


Fig. 12.2. Preparation of phosphorus pentachloride.

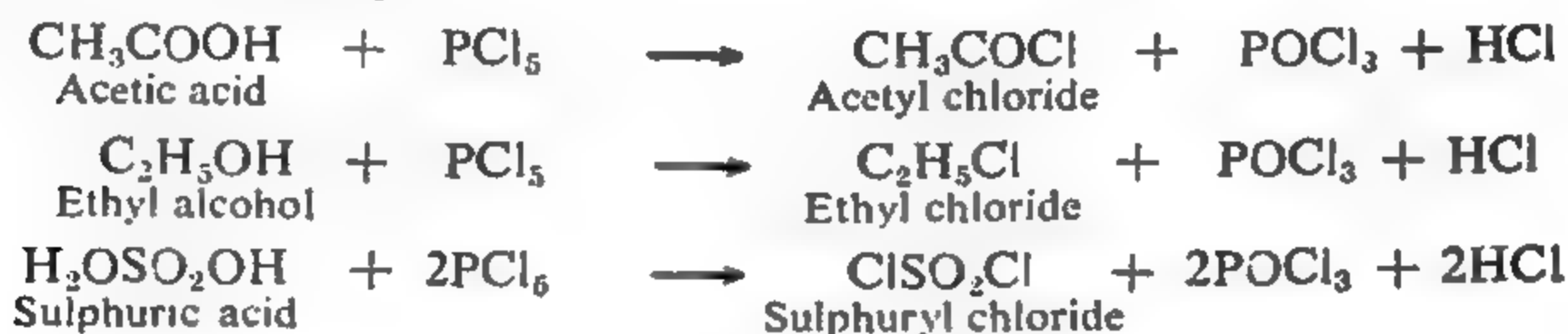
Chemical Properties. 1. Phosphorus pentachloride dissociates on heating into phosphorus trichloride and chlorine.



2. It is violently hydrolysed by water giving phosphorus oxychloride or phosphoric acid depending upon the quantity of water.



3. It reacts with compounds containing hydroxyl groups forming chloro-derivatives. In all these cases, the hydroxyl group is replaced by chlorine. For example,



PHOSPHORIC ACIDS

Phosphorus gives three important phosphoric acids. These are :

- | | |
|---------------------------------|----------------------------------|
| (1) <i>Orthophosphoric acid</i> | H_3PO_4 |
| (2) <i>Pyrophosphoric acid</i> | $\text{H}_4\text{P}_2\text{O}_7$ |
| (3) <i>Metaphosphoric acid</i> | HPO_3 |

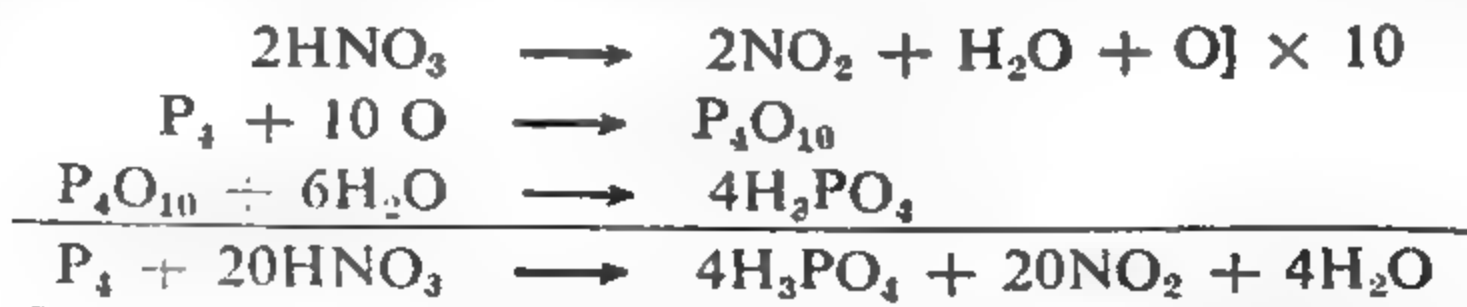
Orthophosphoric Acid, H_3PO_4 .

Preparation. Orthophosphoric acid is prepared :

(1) By carefully dissolving phosphorus pentoxide in water and then boiling the solution.



(2) By the oxidation of red phosphorus with concentrated nitric acid. A crystal of iodine is added to catalyse the reaction (*laboratory method*).



The resulting solution is evaporated, keeping temperature below 180° . The syrupy liquid obtained is allowed to cool in a desiccator when colourless crystals of phosphoric acid are obtained.

(3) By the hydrolysis of phosphorus penta-chloride.



(4) By the action of sulphuric acid on phosphate rock or bone ash (*manufacture*).

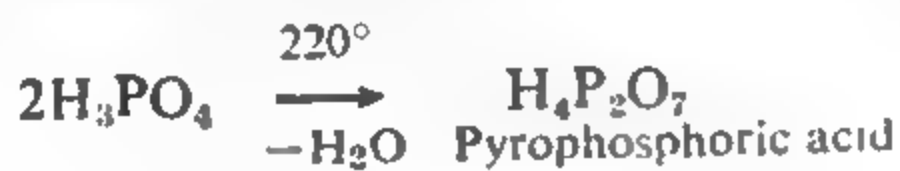


Calcium sulphate being insoluble is removed by filtration and the solution of phosphoric acid concentrated to a syrupy liquid.

Physical Properties. Pure phosphoric acid is a colourless crystalline solid melting at 42.3° . Usually, it is available in the form of a syrupy liquid.

Chemical Properties. (1) Phosphoric acid is a tribasic acid and forms three series of salts with alkalis. For instance, with sodium hydroxide, it gives three salts, NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4 .

(2) On heating up to 220° , it decomposes to give pyrophosphoric acid which, on further heating to 600° , gives metaphosphoric acid.



(3) Phosphoric acid is very stable and possesses no oxidising properties below $350 - 400^\circ$. It is, therefore, used in place of sulphuric acid in the preparation of hydrogen bromide and hydrogen iodide from potassium bromide and potassium iodide respectively.



Orthophosphates or Phosphates.

Orthophosphoric acid, being tribasic, forms three series of salts with alkalis. These are named as primary, secondary or tertiary salts depending upon whether one, two or three hydrogens are replaced by the basic ions. For example, with sodium hydroxide the three salts obtained are :

(i) NaH_2PO_4 , Sodium dihydrogen phosphate or primary sodium phosphate.

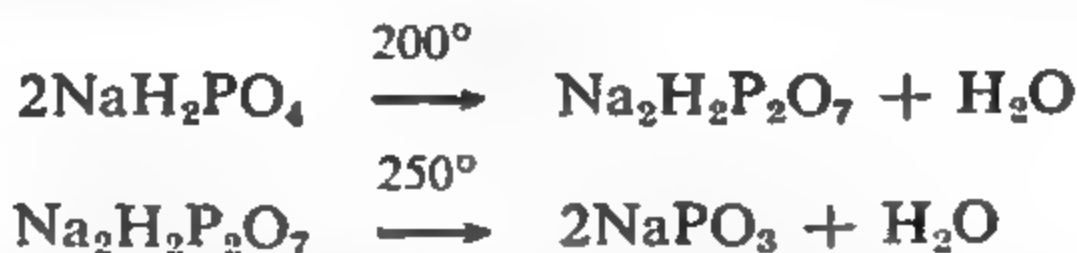
(ii) Na_2HPO_4 , Disodium hydrogen phosphate or secondary sodium phosphate.

(iii) Na_3PO_4 , Trisodium phosphate or tertiary sodium phosphate or normal sodium phosphate.

(i) **Sodium dihydrogen phosphate, NaH_2PO_4 .** It is slightly acidic towards litmus and neutral towards methyl orange. It may be prepared by adding a calculated amount of phosphoric acid to disodium hydrogen phosphate.



Sodium dihydrogen phosphate when heated at 200° , decomposes to give *sodium hydrogen pyrophosphate* which on further heating to 250° , gives *sodium metaphosphate*.



(ii) **Disodium hydrogen phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.** It is neutral towards phenolphthalein and slightly alkaline towards litmus. It may be prepared by adding sodium hydroxide or sodium carbonate solution to phosphoric acid till the solution becomes neutral towards phenolphthalein.



Disodium hydrogen phosphate, on heating to 300° , decomposes to give *sodium pyrophosphate*.



(iii) **Normal sodium phosphate, Na_3PO_4 .** It is strongly alkaline due to hydrolysis. It may be prepared by adding a requisite amount of sodium hydroxide to disodium hydrogen phosphate solution.



Sodium ammonium hydrogen phosphate, $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ or Microcosmic salt. It may be prepared by dissolving ammonium chloride and disodium hydrogen phosphate in the ratio of 1 : 6 (by weight) in a little hot water. The solution on cooling deposits crystals of microcosmic salt.



Microcosmic salt on heating decomposes to give ammonia and sodium metaphosphate.



Microcosmic salt is used in "microcosmic bead test" in qualitative analysis.

Tests of Phosphates

1. *Ammonium molybdate test.* When warmed with an excess of ammonium molybdate solution in the presence of nitric acid, a yellow precipitate of ammonium phosphomolybdate $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 6\text{H}_2\text{O}$, is obtained.

2. *Ferric chloride test.* Ferric chloride, when added to a neutral solution gives a buff coloured precipitate of ferric phosphate, FePO_4 which is soluble in hydrochloric acid but insoluble in acetic acid.

3. *Silver nitrate test.* Silver nitrate, when added to a neutral solution, gives a yellow precipitate of silver phosphate, Ag_3PO_4 . This precipitate is soluble in nitric acid as well as in ammonia.

4. *Magnesia mixture test.* Magnesia mixture (a mixture of MgSO_4 containing NH_4Cl and NH_4OH) gives a white precipitate of magnesium ammonium phosphate.

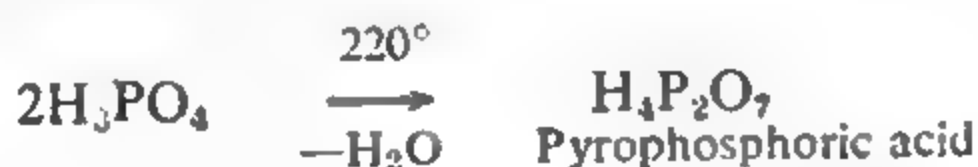


5. *Cobalt nitrate test.* Cobalt nitrate when added to a neutral solution gives a violet blue precipitate which is soluble in acetic acid.

6. *Calcium chloride test.* Calcium chloride, when added to a neutral solution gives a white precipitate of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, which is soluble in acetic acid.

Pyrophosphoric Acid, $\text{H}_4\text{P}_2\text{O}_7$

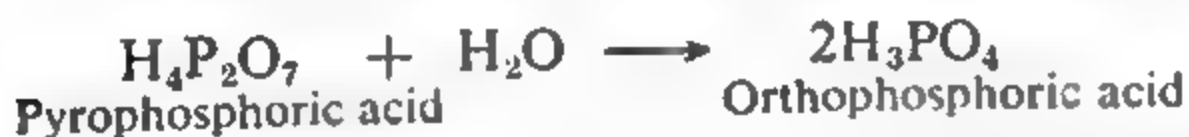
Preparation. Pyrophosphoric acid is usually prepared by heating orthophosphoric acid at 220° .



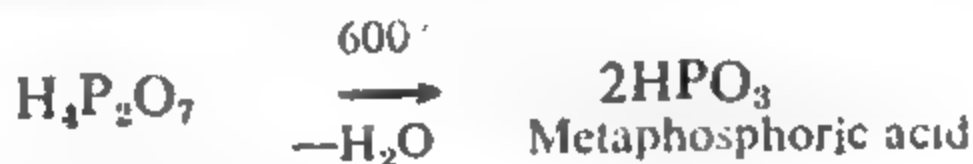
Physical Properties. Pyrophosphoric acid is a colourless crystalline solid melting at 61° .

Chemical Properties. 1. Pyrophosphoric acid is a tetrabasic acid but it gives only two series of salts. Thus, with sodium hydroxide, it gives only the normal salt, sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$ and the dihydrogen salt, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$.

2. It reacts with water giving orthophosphoric acid.



3. On heating upto 600° , it decomposes to give metaphosphoric acid.



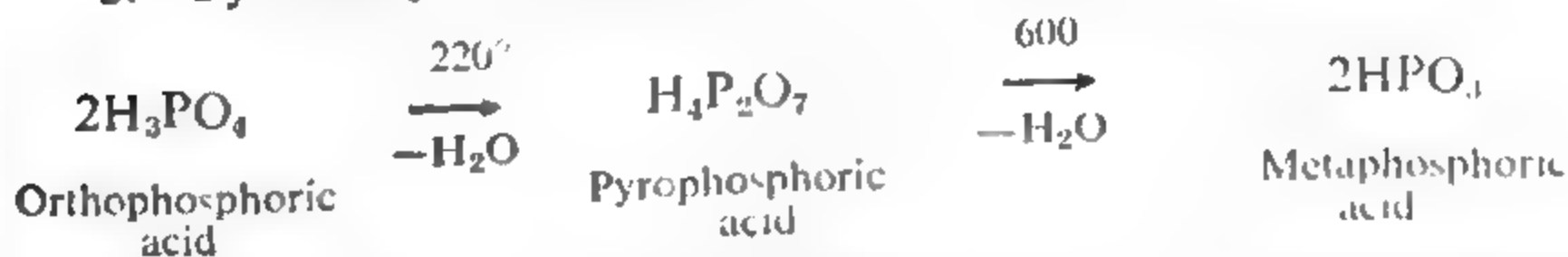
Metaphosphoric Acid, HPO_3

Preparation. Metaphosphoric acid may be prepared :

1. By the action of cold water on phosphorus pentoxide.



2. By heating orthophosphoric acid or pyrophosphoric acid at 600° .



Physical Properties. Metaphosphoric acid is a transparent glossy solid which does not possess a sharp melting point.

Chemical Properties. 1. Metaphosphoric acid is a monobasic acid and forms only one series of salts called *metaphosphates*.

2. It is deliquescent in nature. Its aqueous solution changes into orthophosphoric acid slowly at room temperature and rapidly on heating.

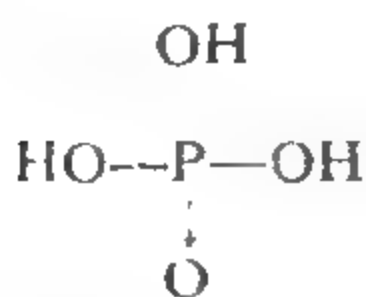


Reactions to distinguish between ortho, pyro, and metaphosphoric acids and phosphates.

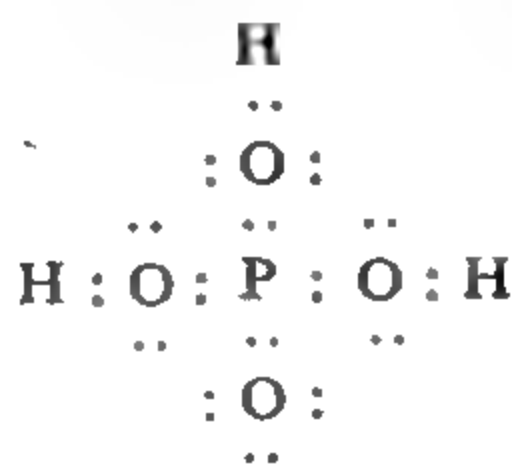
Reagent	H_3PO_4 or Orthophosphates	$\text{H}_4\text{P}_2\text{O}_7$ or Pyrophosphates	HPO_3 or Metaphosphates
1. Silver nitrate (neutral)	Yellow ppt. of Ag_3PO_4	White crystalline ppt. of $\text{Ag}_4\text{P}_2\text{O}_7$	White gelatinous ppt. of AgPO_3
2. Magnesia mixture	White ppt. insoluble in excess of the reagent.	White ppt. soluble in excess of the reagent	No ppt.
3. Cobalt nitrate (neutral)	Violet blue ppt.	Pink ppt.	No ppt.
4. Cadmium chloride and acetic acid	—	White ppt.	—
5. White of egg	No action	No action	Coagulation

Structure of Phosphoric Acids. The three phosphoric acids have been assigned the following structures :

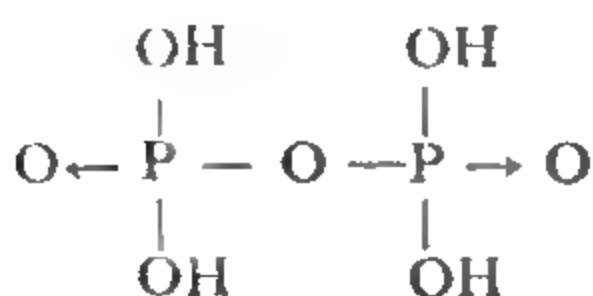
Orthophosphoric acid.



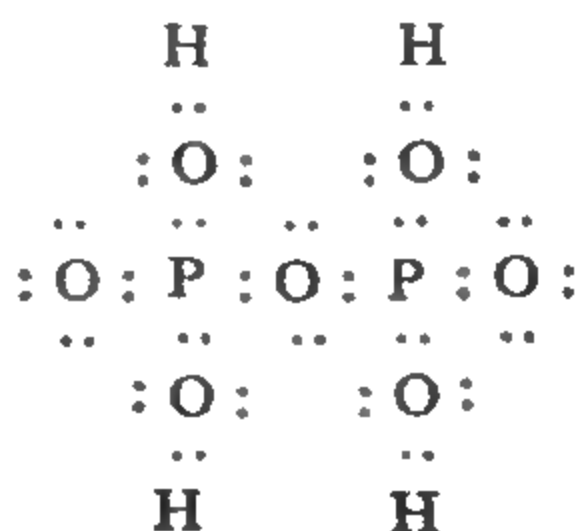
or



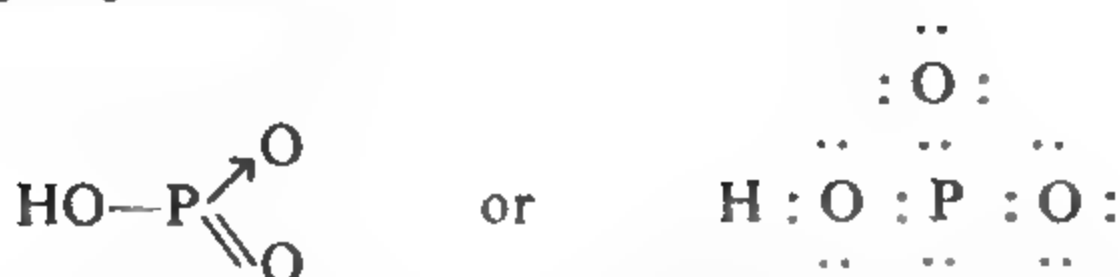
Pyrophosphoric acid.



or



Metaphosphoric acid.



QUESTIONS

1. How is phosphorus trichloride prepared in the laboratory ? Discuss its important properties.
2. Describe the laboratory preparation of phosphorus pentachloride. What happens when phosphorus pentachloride is reacted upon by water, ethyl alcohol and acetic acid ?
3. How is orthophosphoric acid prepared ? What products are obtained on heating orthophosphoric acid ? Give the important tests for phosphates.
4. How is orthophosphoric acid prepared from (i) bone ash (ii) phosphorus, and how is it converted into the other two acids ? What tests may be used to identify these acids ?
(*Panjab Inter 1941, Rajputana Inter 1951, 1952*)
5. How would you distinguish between an orthophosphate and a metaphosphate ? Give equations where necessary.
(*Panjab Inter 1951*)
6. Give the names, formulae and structures of phosphoric acids. How would you distinguish between them ?
7. How would you convert ?
 - (1) Orthophosphoric acid into pyrophosphoric acid and vice versa ?
 - (2) Orthophosphoric acid into metaphosphoric acid and vice versa ?
 - (3) Phosphorus into orthophosphoric acid and vice versa ?

CHAPTER XIII

OXIDES OF CARBON

Carbon forms a number of oxides such as C_4O_3 , C_8O_3 , $C_{12}O_9$, C_3O_2 , CO and CO_2 . Out of these, the most common and the most important are CO and CO_2 .

CARBON MONOXIDE, CO

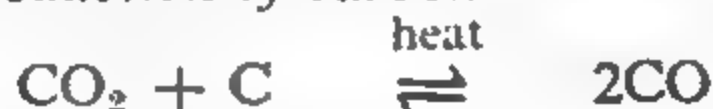
Occurrence. Carbon monoxide occurs in small quantities in volcanic gases, chimney gases, exhaust gases of automobile engines and coal gas.

Preparation. Carbon monoxide may be prepared by the following methods :

(1) *By the reduction of oxides of heavy metals with carbon.* For example,



(2) *By the reduction of carbon dioxide with carbon.*



Carbon dioxide is passed through a silica tube packed with charcoal and heated to red heat. The resulting product is a mixture of CO and CO_2 from which CO_2 is eliminated by passing through caustic soda.

(3) *By the reduction of carbon dioxide with zinc or iron.*

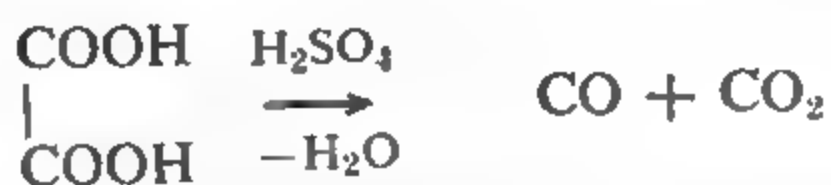


CO_2 is passed over red hot zinc dust or iron filings and the resulting gases are scrubbed with caustic soda to eliminate any CO_2 .

(4) *By heating calcium, barium or magnesium carbonate with zinc or iron filings.*

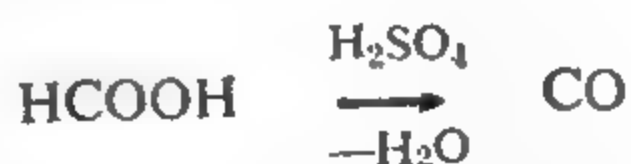


(5) *By heating oxalic acid with sulphuric acid, the latter acting as a dehydrating agent.*



The carbon dioxide is absorbed by passing through caustic soda or caustic potash.

(6) *By heating formic acid with sulphuric acid, the latter acting as a dehydrating agent.*

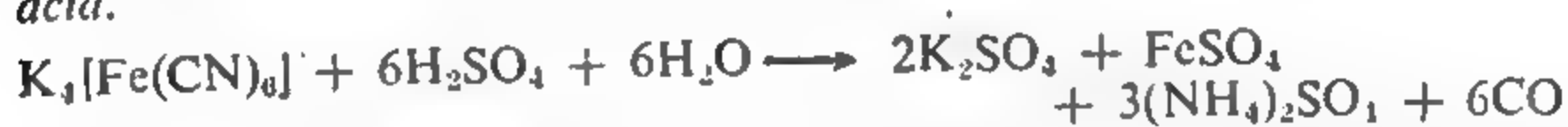


(7) *By the action of steam on heated carbon.*



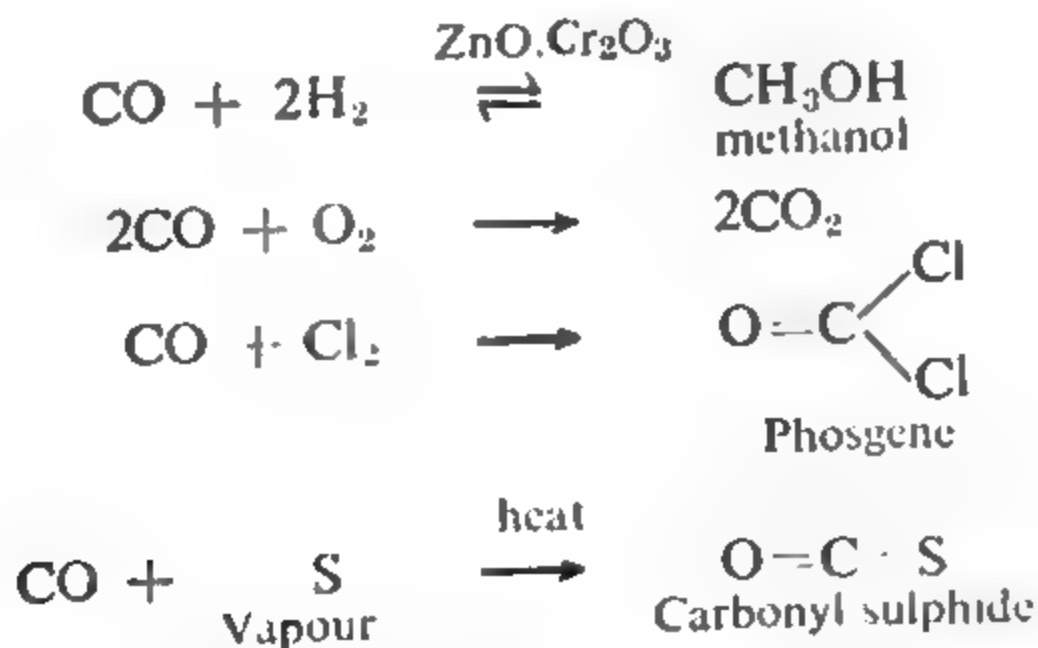
Carbon monoxide is separated by liquefaction. The method is employed for the industrial preparation of monoxide.

(8) *By heating potassium ferrocyanide with concentrated sulphuric acid.*



Physical Properties. Carbon monoxide is a colourless, odourless gas, only slightly soluble in water. It is highly poisonous. One part of the gas in 500 parts of air produces unconsciousness in about an hour and one part in 100 parts will cause death in a few minutes. It liquefies at -191.5° and solidifies at -200° . Its critical temperature is -138.7° .

Chemical Properties. Carbon monoxide, as is evident from its structure, is an unsaturated compound and hence it forms addition products with hydrogen, oxygen, chlorine, sulphur, giving useful products. Thus :



(2) Carbon monoxide is absorbed by sodium hydroxide under pressure giving sodium formate :



(3) Carbon monoxide combines with many metals such as iron, cobalt, nickel, etc., forming carbonyls, for example, $\text{Ni}(\text{CO})_4$, $\text{Co}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, etc.



(4) Carbon monoxide is readily absorbed by a solution of cuprous chloride in concentrated hydrochloric acid or ammonia. This is supposed to be due to the formation of complex ion, $[\text{Cu}(\text{CO})\text{Cl}_2]$ or $[\text{Cu}(\text{CO})\text{NH}_3]^+$.

(5) Carbon monoxide is a good reducing agent. Thus, it reduces zinc oxide to zinc and iodine pentoxide to iodine :



Its tendency to reduce lies in its tendency to get easily oxidised to carbon dioxide.

Tests. Carbon monoxide may be detected by the following tests :

- (i) A filter paper dipped in PdCl_2 solution is turned pink, green or black.
- (ii) Iodine pentoxide gives iodine which imparts violet colour to carbon disulphide.



Uses. 1. It is an essential constituent of fuel gases like water gas, producer gas, etc.

2. It is used in the manufacture of methyl alcohol by its reaction with hydrogen at 300 , under a pressure of 300 atmospheres in the presence of zinc oxide mixed with a little chromium oxide.



3. It is used in the manufacture of sodium formate and formic acid, as shown above.

4. It is also used in metallurgical operations in reducing metallic oxides to metals, e.g.,

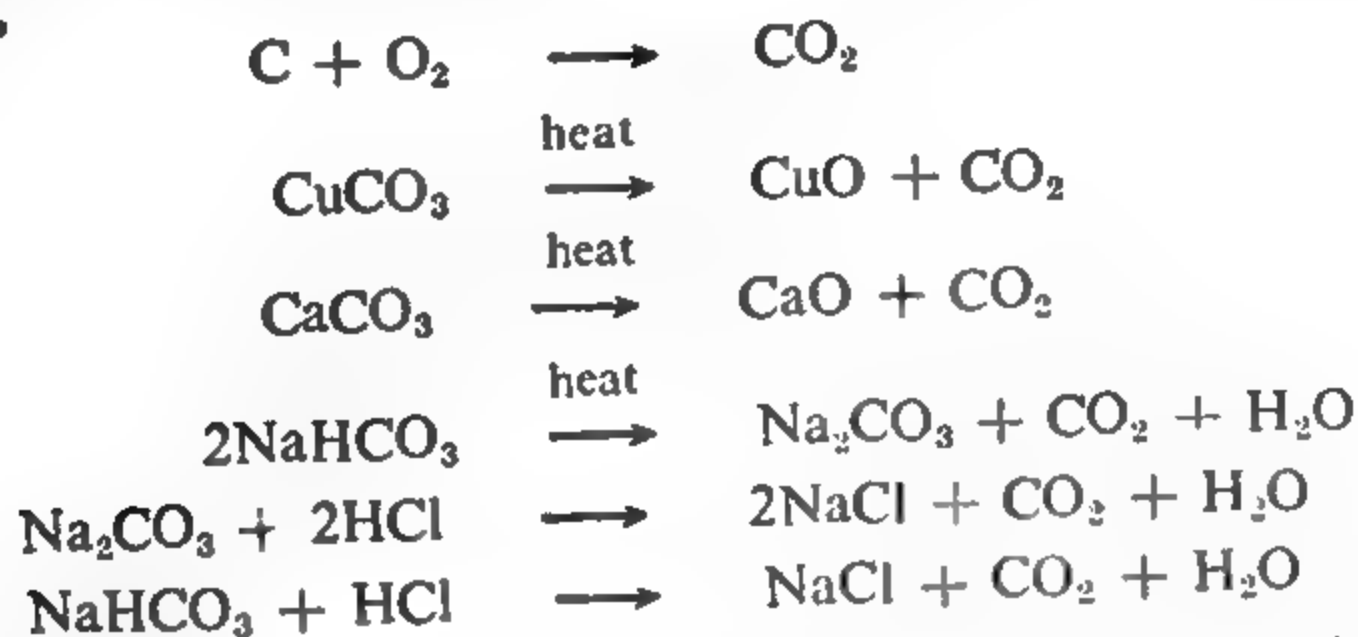


CARBON DIOXIDE, CO_2

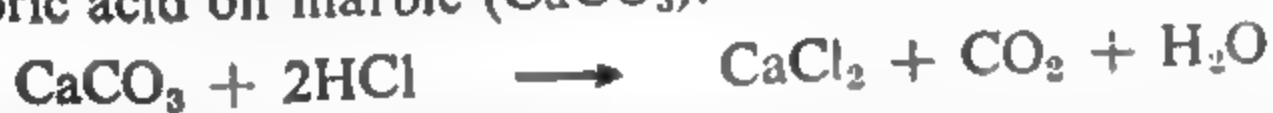
Occurrence. Carbon dioxide occurs in free state to the extent of about 0.03 – 0.05 per cent in the atmosphere. This carbon dioxide results from animal breathing, decay of vegetable matter, burning, etc. In combined state, it is present in carbonate minerals, e.g., *limestone*, CaCO_3 , *dolomite*, CaCO_3 , MgCO_3 , etc.

Preparation. Carbon dioxide may be prepared by the complete combustion of carbon or by the action of heat or dilute acids on carbonates and bicarbonates.

Thus,



In the *laboratory*, the gas is prepared by the action of cold, dilute hydrochloric acid on marble (CaCO_3).



Manufacture 1. From Combustion Gases. The gases produced during the combustion of coal or coke contain large amounts of carbon-dioxide and nitrogen mixed with carbon monoxide, oxygen and other gases or vapours in comparatively smaller amounts. Carbon dioxide is recovered by passing the hot gases up a tower packed with coke down which a solution of potassium carbonate is being sprayed. Carbon dioxide is absorbed giving potassium bicarbonate.



The solution is boiled when carbon dioxide is liberated, the above reaction now being reversed.



The solution containing potassium carbonate can be used again for absorbing carbon dioxide.

2. From Lime-kilns. Carbon dioxide is obtained on a large scale as a by-product in the calcination of limestone (CaCO_3) in the manufacture of lime (CaO).



The gas can be recovered and purified by absorbing it in a solution of potassium carbonate, as described above.

3. From Fermentation Industries. Large amounts of carbon dioxide are obtained as by-product during the fermentation of starch or sugar in the manufacture of alcohol.

Physical Properties. Carbon dioxide is a colourless gas with a faint pungent odour and slight acid taste. Under ordinary pressures, the gas is only slightly soluble in water but at high pressures the solubility increases appreciably.

Carbon dioxide when allowed to issue out of a cylinder, into a flannel bag tied to the nozzle of the cylinder, produces solid carbon dioxide, as a result of intense cooling (*Joule-Thomson effect*). This solid carbon dioxide sublimates at -78.5° and hence the name **dry ice**. With ether it forms an excellent freezing mixture giving as low a temperature as -110° . Carbon dioxide can be liquefied by cooling under a pressure of about 56 atmospheres at 20° . Its critical temperature is 31.1° .

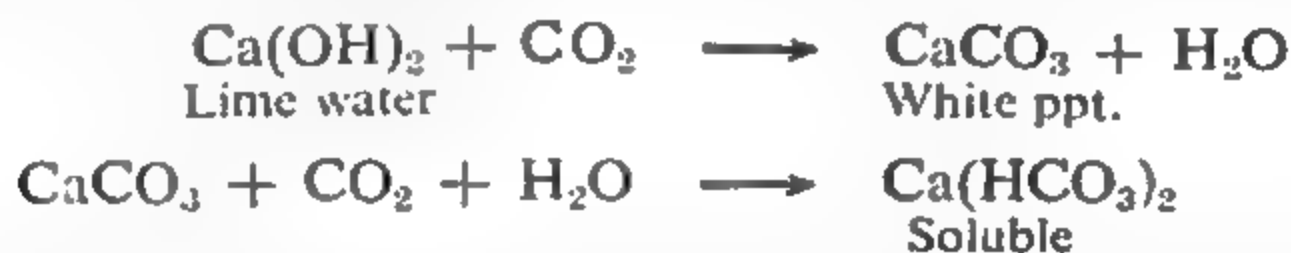
Chemical Properties. Carbon dioxide dissolves in water to a small extent giving carbonic acid and hence it behaves as a weak acid and forms salts with alkalies.



With excess of CO_2 , the carbonate is converted into bicarbonate :



Similarly, with lime water, it gives a white precipitate due to the formation of insoluble calcium carbonate which dissolves as bicarbonate on passing a further quantity of the gas.



Carbon dioxide is neither combustible nor a supporter of combustion. Thus, a burning splinter when introduced into the gas, gets extinguished.

But, burning magnesium, sodium or potassium continues burning in the gas resulting in the decomposition of the gas, to give carbon.



When heated with red hot charcoal it is reduced to carbon monoxide.



Under the action of chlorophyll and sunlight, the plants take up carbon dioxide and liberate oxygen with the simultaneous production of starch and other carbohydrates. The process is known as **photosynthesis**.



Uses. (i) It is used in extinguishing fire. There are two kinds of fire-extinguishers. The first type, known as the **acid-soda type**, consists of a strong iron vessel containing concentrated solution of sodium bicar-

bonate. A small glass bottle containing sulphuric acid is held inside the vessel. At the time of use, the apparatus is inverted and hit against the ground when the cork of the glass bottle breaks down and the acid falls into the bicarbonate solution. A swift reaction, evolving carbon-dioxide forcefully from the nozzle of the apparatus, takes place.

In the second type, known as the **foamite fire extinguisher**, instead of sulphuric acid, a solution of aluminium sulphate (or potash alum) contained in a glass cylinder, is used. The reaction with sodium bicarbonate, gives not only carbon dioxide but also a fine precipitate of aluminium hydroxide.



Aluminium hydroxide comes out along with carbon dioxide as a rich foam. While carbon dioxide helps in extinguishing the fire, aluminium hydroxide deposits itself on the burning articles and thus cuts off their contact with the air.

(ii) Carbon dioxide is used in aerated waters. The advantage is taken of its increased solubility in water under pressure.

(iii) Solid carbon dioxide (*dry ice*) is used in freezing mixtures giving very low temperatures and as a germicide.

(iv) A mixture containing 97 per cent oxygen and 3 per cent carbon dioxide is used for artificial respiration.

QUESTIONS

1. Describe the various methods for the preparation of carbon monoxide. Discuss its important properties and uses.

2. How is carbon monoxide prepared? Explain how can it be converted into (1) methyl alcohol (2) Phosgene (3) Formic acid (4) Carbon dioxide. What tests would you apply for the gas?

3. Describe the various methods for the preparation of carbon dioxide. Discuss its important properties and uses.

4. How is carbon dioxide prepared on a large scale? To what industrial uses can this be put?

5. Describe the laboratory preparation of carbon dioxide. How can it be converted into carbon monoxide? Discuss the reducing properties of carbon monoxide.

6. How is carbon dioxide obtained from (1) Lime (2) Coal? What is dry ice and to what use is it put? Discuss the use of carbon dioxide as a fire extinguisher.

CHAPTER XIV (A)

SILVER

History. Silver has been known since the ancient times. It was called *luna* and was represented by a symbol as for the crescent moon. Romans called it *argentine* which has given the symbol Ag to the metal.

Occurrence. Silver occurs native in a few places in Canada, United States of America and Mexico with varying amounts of copper and gold. Its most important ores are :

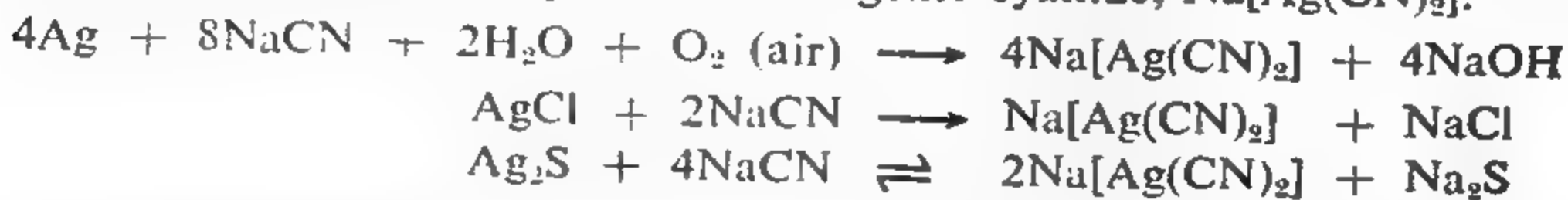
<i>Argentite (silver glance)</i>	Ag_2S
<i>Horn silver</i>	AgCl
<i>Pyrargyrite (Ruby silver)</i>	Ag_3SbS_3

The ores are mixed with a large amount of rock, silica and clay. The silver content hardly exceeds 1 per cent.

Lead and copper ores are generally contaminated with silver. Argentiferous galena (PbS) contains 0.01 to 0.1% silver. The anode mud from copper refineries also contains workable quantities of silver.

Extraction. There are many processes for the extraction of silver from various ores. The chief of these are as follows :

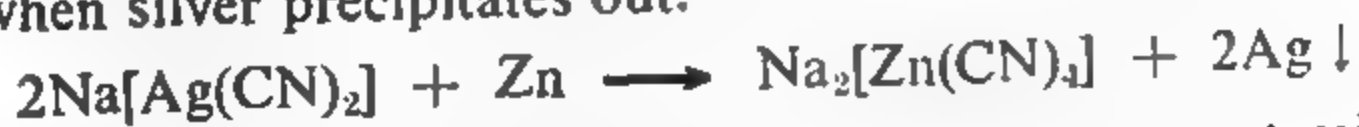
1. **Cyanide process.** In this process the finely powdered ore is leached for several hours with a dilute (0.5%) solution of sodium cyanide, the mixture being all the while agitated by a current of air. Metallic silver chloride and silver sulphide all pass into solution with the formation of the complex sodium argento cyanide, $\text{Na}[\text{Ag}(\text{CN})_2]$.



Sodium sulphide is at the same time largely oxidized to sodium sulphate by the air current.



The solution containing the silver complex is removed and treated with zinc dust when silver precipitates out.



The precipitated silver is finally fused with borax or potassium nitrate to purify it.

2. Desilverization of lead. The lead obtained from galena (PbS) contains about one per cent of silver which can be profitably isolated by the following processes :

(i) **Pattinson process.** The molten argentiferous lead is cooled slowly when crystals of lead gradually separate out in stages and the melt progressively becomes richer and richer in silver until it contains 2.6% silver when an eutectic mixture of this composition solidifies at 303° . Pattinson's method for the desilverisation is now practically obsolete.

(ii) **Parke's process.** This process is superior to Pattinson's process and is now largely employed. It is based on the fact that silver is more soluble in molten zinc than in molten lead while molten zinc and molten lead are practically immiscible. The argentiferous lead is melted and thoroughly mixed with 1 to 2 per cent of zinc. After some time the molten zinc rises to the top carrying almost the whole of silver with it. On cooling, zinc solidifies first and is skimmed off with perforated spoons while the lead is still in molten state. The zinc-silver alloy is heated first moderately so as to melt any lead adhering to it and then strongly in clay retorts when zinc distils off leaving silver behind.

The silver obtained above still contains some lead as impurity. It is melted and strongly heated in a *cupel* which is a shallow dish of bone-ash placed on the removable hearth of a reverberatory furnace

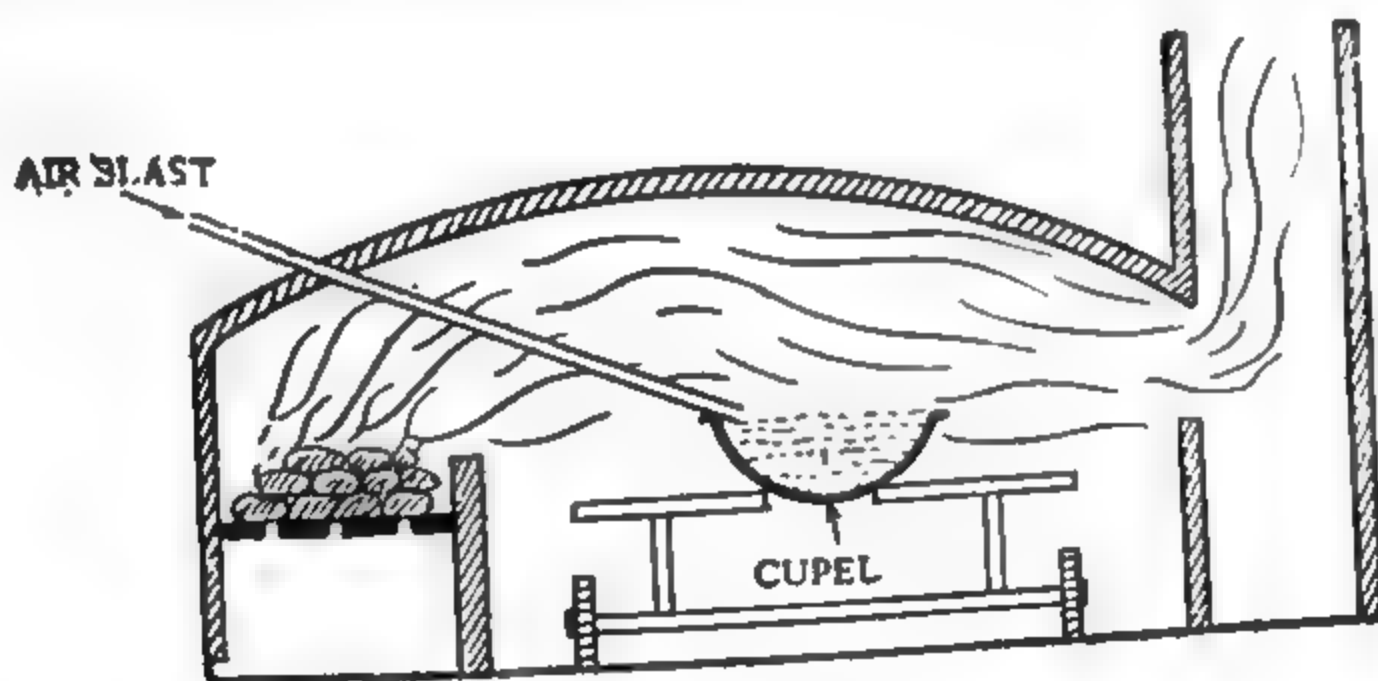


Fig. 14(A).1. Cupellation.

(Fig. 14(A).1) under a blast of air. Lead is oxidised to litharge, PbO , which is removed by air and the shining surface of silver appears. This step is called **cupellation**.

Purification of Silver. The silver to be refined is converted into blocks and made the anodes of an electrolytic cell. Cathodes used are made

of pure silver. A dilute solution of silver nitrate, with about 1% nitric acid, serves as the electrolyte. During electrolysis, silver dissolves from the anodes and is deposited on the cathodes. Any impurity of copper in the anodes dissolves in the cathodes, while the gold remains undissolved and is deposited as a slime. The solution in the cell is changed if the copper present in it exceeds 4—5 per cent.

Physical Properties. Silver is a white lustrous metal, highly malleable and ductile. It is the best conductor of heat and electricity. It has a density of 10.5 and melts at 960.8° . Molten silver can absorb oxygen which is given off on cooling causing violent spurting. This phenomenon is called *spitting of silver*.

Chemical Properties. Silver has a poor chemical activity. Therefore, it is known as a *noble* metal. Following are its chief chemical properties :

(i) **Action with air.** Silver is not attacked by air or moisture. But when exposed to the air containing even traces of hydrogen sulphide, it turns black due to the formation of a thin layer of silver sulphide on its surface.

(ii) **Action with halogens.** When heated strongly in a current of halogen gas or vapour, it forms the corresponding halides, e.g.,



(iii) **Action with sulphur.** Silver has great affinity for sulphur. When heated with sulphur powder, it forms silver sulphide.



(iv) **Action of acids.** Silver is not attacked by non-oxidizing acids, i.e., hydrochloric acid and dilute sulphuric acid. However, it reacts with nitric acid and concentrated sulphuric acid forming silver nitrate and silver sulphate respectively.



It is not attacked by *aqua regia*. Advantage is taken of this fact in separating it from gold (which is attacked by *aqua regia*).

(v) **Action of alkali cyanides.** Silver dissolves in sodium cyanide or potassium cyanide in the presence of air, due to the formation of the complex argentocyanide ion.



Uses of Silver. (1) Silver is used in coins ornaments, silver ware, decoration pieces, etc. As silver itself is rather soft, for most purposes it is alloyed with copper. The silver alloy used for ornaments contain about 80 per cent silver and 20 per cent copper.

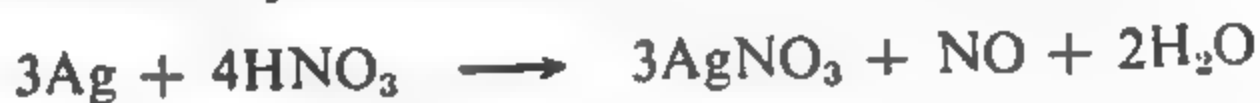
(2) Silver is used in plating articles made of baser metals. The article to be silver-plated is made the cathode while the anode consists of pure silver. The bath contains a solution of potassium argento-cyanide, $K[Ag(CN)_2]$. As the complex ion is very stable, the concentration of silver ion (Ag^+) in solution is very small at any time.



Therefore, silver is deposited more slowly and uniformly than from a solution of silver nitrate.

(3) Its compounds are used in silvering of mirrors and in photography.

Silver Nitrate, $AgNO_3$. This is the most important compound of silver. It is obtained by dissolving silver in dilute nitric acid.



On evaporating the solution, colourless crystals of silver nitrate are deposited.

Silver nitrate, when pure, is not decomposed by light but when it is deposited on an organic matter such as paper or cloth or skin, it is reduced to silver. It is, therefore, used in marking clothes where it leaves a mark of black silver on the material. When rubbed on the skin, it leaves a black deposit. It is, therefore, used as a mild caustic in surgery. Hence, it is also known as *lunar caustic*. It is soluble in water.

On heating, it decomposes giving nitrogen dioxide and oxygen.



It forms the complex $[Ag(NH_3)_2]^+$ when dissolved in aqueous ammonia. In this form, it is readily reduced to metallic silver by organic reducing compounds. Ammoniacal silver nitrate is, therefore, used in testing for aldehydes, formates, and glucose, as well as in the silvering of mirrors.

When acetylene is passed through ammoniacal silver nitrate a white precipitate of silver acetylide is formed.



Silver nitrate is used as a valuable laboratory reagent in qualitative as well as quantitative analysis. It gives precipitates with halides (except fluorides), cyanides, chromates, phosphates, etc. When silver nitrate is added to a neutral solution of an organic acid, the insoluble silver salt of the acid is obtained. On igniting, it leaves a deposit of metallic silver. This reaction provides a method for determining equivalent weights of organic acids. Silver nitrate is used in gravimetric analysis for estimating chloride ions and in volumetric analysis for estimating chloride, bromide and cyanide ions.

Tests for Silver Compounds.

(1) *Charcoal cavity test.* When mixed with sodium carbonate and heated in charcoal cavity, a white bead of silver is obtained.

(2) The addition of hydrochloric acid or any soluble chloride gives a white curdy precipitate of silver chloride readily soluble in ammonia but insoluble in nitric acid.

(3) A neutral solution of a silver salt gives a brick red precipitate of silver chromate, Ag_2CrO_4 , which is soluble both in nitric acid and ammonia.

SILVERING OF MIRRORS

It is the art of deposition of a thin, uniform layer of silver on a clean glass plate. It is based on the reduction of ammoniacal silver nitrate solution by a neutral tartrate or glucose in the cold. A number of recipes are in use.

In one of the processes, two separate solutions are prepared. One solution contains 1.0 gm. of Rochelle salt and 0.25 gm. of silver nitrate dissolved in 500 ml. of water. The solution is boiled until it changes into grey. It is filtered and the volume made up to 750 ml.

The other solution is prepared by dissolving 50 gm. of silver nitrate in 300 ml. of distilled water, adding ammonia gradually until the precipitate formed is just redissolved. The solution is filtered and the volume is made up to 750 ml.

The two solutions are mixed in equal proportions and diluted by an equal amount of water. In the meanwhile, the glass plate to be silvered is thoroughly cleaned by caustic soda (to remove grease), dilute hydrochloric acid and water and then dried. The mixture is then poured over the glass plate to form a thin layer. After some time, silver gets deposited on the plate. It is then washed and dried and finally given a thin protective coating of asphalt varnish or of a paste of red lead in turpentine.

PHOTOGRAPHY

The fact that silver salts are sensitive to the action of light is as old as the sixteenth century. However, the photography in its crude and elementary form started only in the beginning of the nineteenth century, when Herchel made the discovery that silver chloride was soluble in sodium thiosulphate.

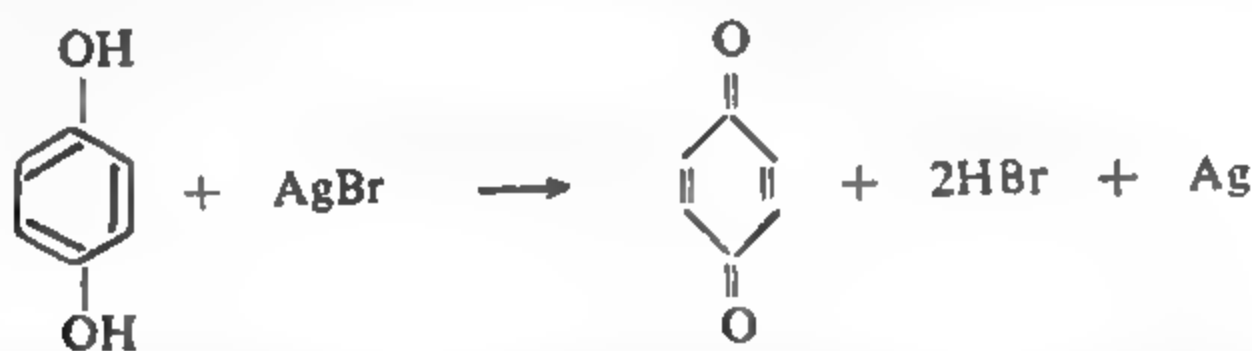
The modern photography involves a number of steps as briefly discussed below :

(1) **Preparation of sensitive plate.** Glass plates (or films of celluloid) are coated with an emulsion of silver bromide in gelatin to get sensitive plates. The emulsion is prepared as follows : A gelatin solution of silver nitrate is mixed with a gelatin solution of ammonium bromide and allowed to stand in a warm place. The process is called *ripening*. The fine particles of the silver bromide precipitate grow bigger and thus become more sensitive to light.

(2) **Exposure.** The sensitive plate is then momentarily exposed, in a camera, to the required object, the exact time of the exposure depend-

ing upon the speed of the plate and the intensity of light. The decomposition of silver bromide into extremely small particles of silver takes place instantaneously. This gives a *latent image* of the object. The number of small particles of silver in a given area of the plate depends upon the intensity of light falling on that area.

(3) **Developing.** The exposed plate having the latent image is then placed in a *developer* which is a mixture of reducing agents such as potassium ferrous oxalate, hydroquinone or an alkaline solution of pyrogallol. The function of the developer is to complete the reaction started by light; the silver produced by light is supposed to act as a catalyst so that the reaction of the developer is more where more light has fallen. Silver bromide is reduced to silver and the plate shows black spots of silver. Gradually, these spots cover more and more area and make a coherent picture in which the bright portions appear dark and vice versa.



Thus, the image becomes visible but there is a reversal of shade, that is, the bright portions of the object appear dark and vice versa. The developed plate is, therefore, called a *negative*.

(4) **Fixing.** The developed plate still contains some unreduced silver bromide which must be removed to avoid 'fogging' (that is blackening of the entire plate on exposure to light). This is done by immersing the plate in a solution of *hypo*, that is, sodium thiosulphate. Silver bromide then disappears on account of the following reaction :

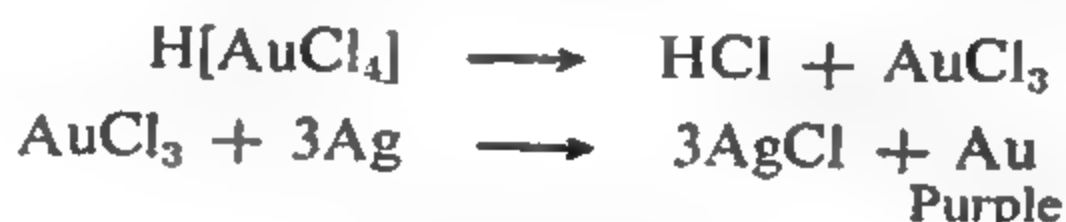


The plate is then thoroughly washed in water and dried. It is now no longer sensitive to light and can be taken out of the dark room and exposed to light.

(5) **Printing.** The *negative* is now placed on a special printing paper in a frame and exposed to light. This paper has a film of silver bromide in gelatin similar to that on a photographic plate, deposited on it. When light passes through the *negative* and comes in contact with the paper, decomposition of silver bromide resulting in the deposition of extremely minute particles of silver takes place. As the brighter areas of the negative permit the passage of more light through them, there will be greater decomposition of silver on the corresponding areas of the paper which will, therefore, appear as dark. The darker areas of the negative, on the other hand, will permit the passage of less light through them, and consequently the corresponding areas on the paper will appear brighter in comparison. In this way, we get on the

paper a negative of the negative, that is, a positive print of the original object. The paper is then developed and fixed in the same manner as the negative.

(6) **Toning.** In order to obtain better effects, the prints are 'toned' by dipping in 'gold chloride', HAuCl_4 , or potassium platinichloride, K_2PtCl_6 solution when silver goes in solution and a beautiful purple tint or steel grey tint is imparted to the photograph due to the deposit of gold or platinum as the case may be :



ELECTROPLATING

Electroplating is an art of depositing a superior or a more noble metal on an inferior or a baser metal by means of electrolysis of an aqueous solution of a suitable electrolyte. For example, metals like iron which are easily corroded by atmospheric air, moisture and carbon dioxide, are coated electrolytically with deposits of nickel or chromium which are more resistant to chemical attack. Picture frames and machinery parts are often chromium-plated to protect them from corrosion and at the same time to give them a good polish.

Sometimes, electroplating is done with a view to repairing worn out parts of a machinery. In such cases, the suitable metal is deposited electrolytically on the effected parts of the machinery.

Electroplating is also done occasionally for ornamentation and decoration purposes. For example, several articles made of copper or its alloys, such as table wares, decoration pieces, are coated with silver or gold.

The electrolytic deposits are crystalline in nature. The crystals must be very fine in order to get firm, coherent and uniform deposits. For this purpose suitable electrolytes should be used in the electrolytic bath and current density should have an appropriate value. The temperature should also be maintained at a proper level and the articles to be coated with the nobler metals should be in as high a state of purity as possible. These conditions are briefly discussed below :

Electrolytic bath. The electrolyte used in the electrolytic bath depends upon the nature of the metal to be deposited. In **copper plating**, for example, when a coarse crystalline deposit is required, copper sulphate acidified with sulphuric acid is used. But, for finer deposits, an alkaline solution of potassium cuprocyanide, $\text{K}_2[\text{Cu}(\text{CN})_3]$, is used. In **silver plating**, potassium argentocyanide, $\text{K}[\text{Ag}(\text{CN})_2]$, is used as the electrolyte. The substance dissociates in water as under :



The complex ion is highly stable. It dissociates only to a very small extent as :



Consequently, the concentration of silver ions at any time is very low and silver is deposited on the cathode as a coherent film of metal (instead of the crystalline metal formed when silver nitrate is used as the electrolyte). At the same time, the silver ion concentration in the solution remains more or less constant as electrolysis proceeds.

For the same reason, in **gold plating**, the bath consists of a solution of potassium aurocyanide, $\text{K}[\text{Au}(\text{CN})_2]$ or potassium auricyanide, $\text{K}[\text{Au}(\text{CN})_4]$. The complex anion, *e.g.*, $[\text{Au}(\text{CN})_2]^-$ is highly stable and furnishes a very low concentration of gold ions which also remains constant as electrolysis proceeds.

In **chromium plating**, a solution of chromic acid mixed with a small amount of sulphuric acid is used. The chromate ions, CrO_4^{2-} , in this bath are first reduced to chromic ions, Cr^{3+} , which are then discharged at the cathode. As in the case of complex salts of silver and gold, the concentration of chromic ions always remains low and constant so as to give a firm and coherent film of chromium on the article to be chromium plated.

In **nickel plating**, a solution of nickel ammonium sulphate mixed with some ammonium chloride and boric acid is used to get a firm and durable deposit of the metal. Ammonium chloride serves to increase the conductivity while boric acid acts as a buffer to keep the variation in pH values to the minimum.

Current density and temperature. The rate of deposition increases with increase in current density (*i.e.*, current per unit area). However, if current density is increased beyond a certain limit, the deposit is no longer uniform or coherent. Besides, it becomes dark and much coarser crystals are deposited. For a good deposit, it is also necessary that the temperature of the bath should not be outside a certain limit. By experiments, a certain optimum value for current density and temperature have been worked out for each electrolyte. For example, for sodium cuprocyanide bath, the optimum current density lies between 3-6 amperes per square foot and the optimum temperature is 45° . The optimum conditions for sodium argentocyanide bath are 4 ampere, sq. ft. of current density and 20° as the temperature.

Cleaning the metal surface. For smooth, bright and strong deposits, the surface upon which a layer of a noble metal is required, should be thoroughly cleaned first mechanically by grinding or scratching (against a rough surface) or sand blasting and then chemically by treatment with hot alkalis (if the surface is greasy) or with dilute acids (if the surface has oxide films) or with organic solvents.

The metal upon which the deposit is required is made the cathode while the anode consists of the metal (pure) which is to be deposited.

QUESTIONS

1. Name the important ores of silver. Explain how silver is extracted from its ores. How does silver react with hydrochloric acid, sulphuric acid and nitric acid ?

2. Describe the cyanide process for the extraction of silver. How is silver purified ?

3. Describe the extraction of silver from argentiferous lead. Discuss the important properties and uses of the metal.

4. Describe Parke's process for the desilverisation of lead. What is meant by cupellation ?

5. Describe the preparation, properties and uses of silver nitrate.

6. What is lunar caustic ? Why is it so called ? Describe its preparation and properties.

7. Describe in detail the process of photography explaining clearly the function of the developer. What is meant by toning ?

8. Write short notes on :

(1) Electroplating.

(Jammu & Kashmir T.D.C. (I) 1967)

(2) Silvering of mirrors.)

(Jammu & Kashmir T.D.C. (I) 1966)

(3) Cupellation.

9. Name the chief ores from which silver is obtained. Describe the cyanide process for its extraction. How it is refined ? *Jammu & Kashmir T.D.C. (I) 1967)*

CHAPTER XIV (B)

MERCURY

History. Mercury as metal was known even in 300 B.C. when Theophrastus is reported to have obtained it by rubbing cinnabar with vinegar in a brass pestle and mortar. Aristotle refers to it as quick silver. Pliny called it *hydrargyrum*. The present day symbol Hg has been derived from this word.

Occurrence. Small quantities of mercury occur in free condition, disseminated in rocks. Its ore, *cinnabar*, HgS , is found chiefly in Spain and Italy.

Extraction. Cinnabar (HgS) is taken and crushed dry and screened into two grades. The large size pieces, richer in the ore, are sorted and subjected to a combined process of roasting and distillation.



Various types of furnaces have been used for this purpose but important ones are *Idrian furnace* and *Shaft furnace*.

Idrian Furnace. The ore is placed on *perforated arches* of the furnace (Fig. 14(B).1) and is subjected to combustion in a free supply of air. Sulphur dioxide, waste gases and mercury vapours are led to the air-cooled condensing chambers on the sides. The metal condenses in these chambers as liquid and is tapped out. The condensers are on each side.



Fig. 14(B).1. Idrian furnace for the extraction of mercury.

They are interconnected alternately at top and the bottom. The last chamber on each side is cooled by a water spray.

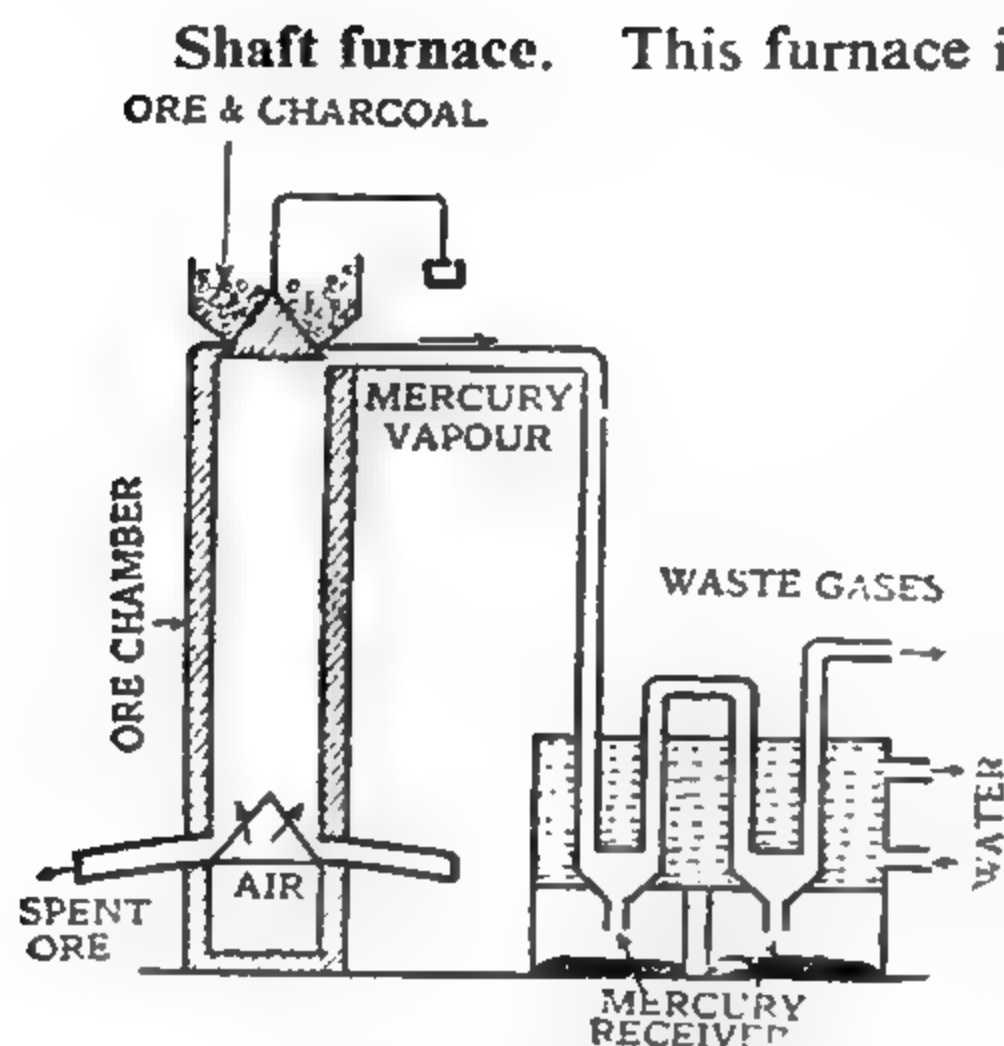


Fig. 14(B).2. Shaft furnace for the extraction of mercury.

Shaft furnace. This furnace is used when the ore is rather poor. It is a continuous process and much more economical as compared to the Idrian furnace. A vertical section of the furnace is shown in Fig. 14.(B)2. It consists mainly of the reaction and condensing chambers. The reaction chamber is fitted with a hopper at the top and a series of sloping shelves which are fitted to the sides of the shafts (not shown in the figure.) The ore mixed with a small quantity of lime is fed from the top and hot gases from the furnace are made to pass in a countercurrent movement of the ore. In the reaction chamber cinnabar decomposes to form mercury metal.



The waste gases along with mercury vapours are led into the condensing chambers, where mercury condenses, and is occasionally removed. Spent ore along with calcium sulphide and calcium sulphate, is removed from time to time from the base of the reaction chamber.

Purification. Mercury thus obtained contains iron and zinc as the main impurities. Some dust particles and mercury oxide are also present in the form of a scum which, however, can be removed by squeezing mercury through chamois leather.

The following methods are employed for further purification :

(1) *Treatment with dilute nitric acid.* Mercury is allowed to drop in a stream of fine droplets through a column (Fig. 14(B) 3) containing dilute nitric acid of 1.1 specific gravity. Some mercurous nitrate is produced which reacts with the metals (zinc, iron, etc.) forming their nitrates (which pass in solution) leaving mercury in pure state. The process is repeated several times to ensure complete removal of the baser metals.

(2) *Vacuum distillation.* Mercury is best purified by distillation. But at ordinary pressure, bumping of mercury is so strong that it is not possible to distil it. However, at reduced pressure distillation is quite convenient. It is conducted in a specially

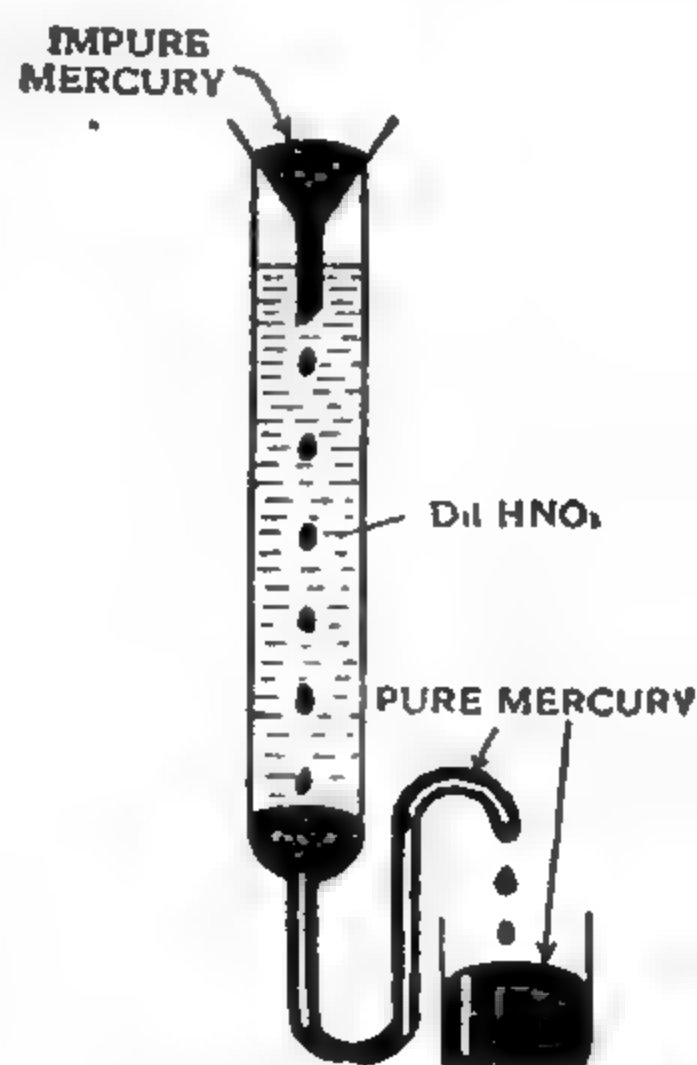


Fig. 14(B).3. Purification of mercury.

designed apparatus where vacuum is maintained automatically. The process is continuous.

Physical Properties. It is a silvery white metal and liquid at ordinary temperatures. It freezes at -38.85° to a crystalline solid which is malleable and ductile. It boils at 357° giving colourless vapour, the density of which shows its molecules to be monoatomic. The vapours in cold do not conduct electricity but when hot they conduct electricity well, giving out characteristic mercury spectrum rich in ultra-violet rays. This is the principle of mercury vapour lamp. It forms amalgams with all metals except iron and platinum.

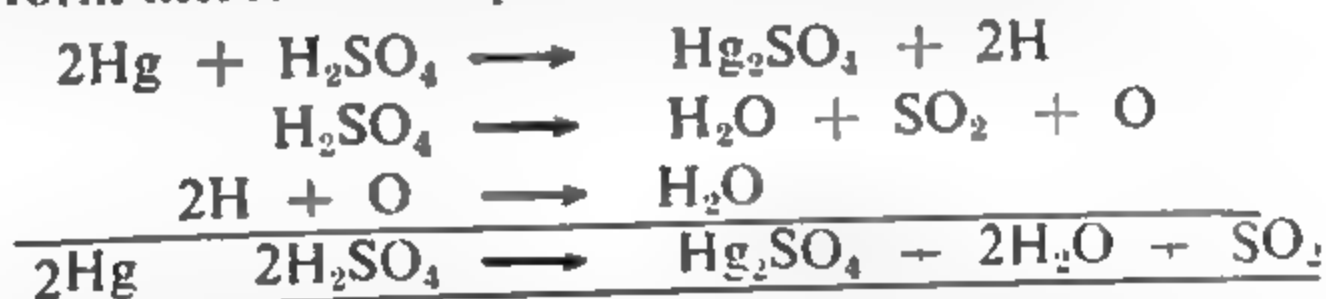
Chemical Properties (1) Action of oxygen. Mercury is not attacked by oxygen or air at ordinary temperatures but when heated above 350° , it slowly combines with oxygen forming mercuric oxide.



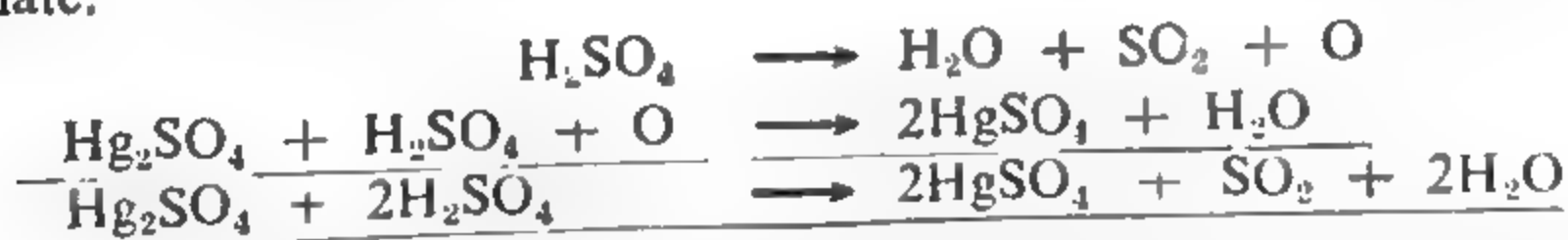
(2) **Action of halogens.** Mercury combines readily with halogens forming the halides, for example,



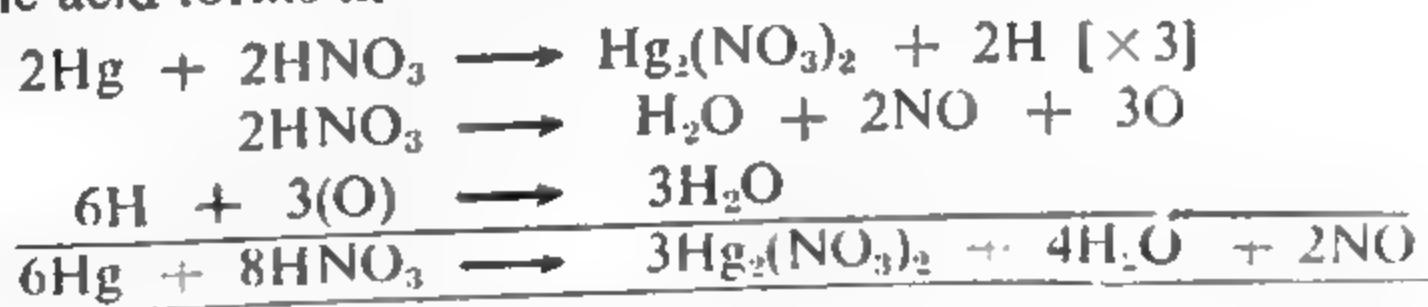
(3) **Action of acids.** Mercury is not attacked by dilute hydrochloric acid and sulphuric acid in cold but hot concentrated sulphuric acid reacts with mercury to form mercurous sulphate and sulphur dioxide.



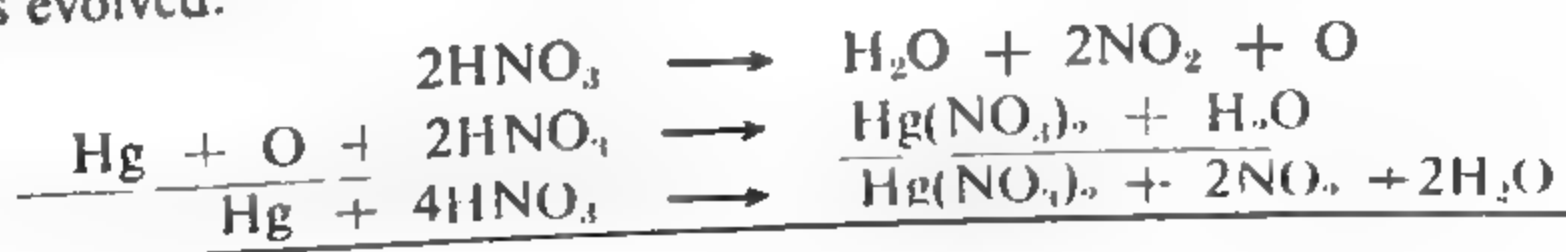
With excess of acid, mercurous sulphate is further oxidised to mercuric sulphate.



The reaction with nitric acid is quite complicated. The products obtained depend upon the temperature and concentration of the acid. Warm dilute nitric acid forms mercurous nitrate and nitric oxide.



With concentrated nitric acid, mercuric nitrate is formed and nitrogen dioxide is evolved.



Uses. It is used for filling thermometers, manometers, vacuum pumps, diffusion pumps, etc. Mercury vapour lamps are used as a source of ultraviolet light. Mercury and its compounds are extensively used in medicine. Amalgams of various metals are used for producing hydrogen at controlled rate. It is used as an electrode in a number of electrolytic processes.

Mercurous Chloride, Calomel, Hg_2Cl_2 . It is prepared by mixing solution of a chloride with a soluble mercurous salt.



It can also be prepared by heating mercuric chloride and mercury in an iron vessel till a white mass is formed. Mercurous chloride thus obtained can be purified by sublimation.



Mercurous chloride or calomel is a white powder without any taste or smell. It is insoluble in water. When heated dry, it sublimes. The vapour on heating decompose to give mercuric chloride and mercury.



On treatment with ammonia it gets blackened. This is due to the formation of a compound of the formula $\text{H}_2\text{N.Hg.HgCl}$.



This compound is unstable and changes into mercury and *mercuric amido-chloride*, $\text{H}_2\text{N-Hg-Cl}$.



Mercurous chloride is used in medicine as a purgative. It is also used in setting up the so-called 'calomel electrode'.

Mercuric Chloride, HgCl_2 . It is obtained by heating mercury in chlorine. Commercially, it is prepared by heating a mixture of mercuric sulphate and sodium chloride and a small amount of manganese dioxide.



Mercuric chloride formed sublimes off. The function of manganese dioxide is to oxidise any mercurous salt formed during the reaction. It is also prepared by dissolving mercuric oxide in hydrochloric acid.



It has a corrosive action and is, therefore, known as **corrosive sublimate**.

Mercuric chloride is a white crystalline compound fairly soluble in water. It is very slightly ionised in water and, therefore, is a poor conductor of electricity. It behaves like a covalent compound and is soluble in organic solvents. It is reduced to mercurous chloride readily by stannous chloride.



If stannous chloride is in excess, mercury is formed.



When aqueous ammonia is added to a solution of mercuric chloride, a white precipitate which is infusible and is known as "infusible white precipitate"—an aminobasic mercuric compound, is formed.



Mercuric chloride is a strong poison. The best antidote is the white of an egg.

TESTS FOR MERCURY COMPOUNDS

1. When a compound of mercury is heated along with sodium carbonate in an ignition tube, mercury separates out as a gray deposit.

2. *Mercurous ions, Hg_2^{++}* (i) When dilute hydrochloric acid is added to the solution of a mercurous salt, a white precipitate is obtained. It is blackened by ammonia.

(ii) The addition of ammonium hydroxide to a mercurous salt gives a black precipitate.

(iii) The addition of stannous chloride, produces a greyish black precipitate of mercury.

3. *Mercuric ions, Hg^{++}* (i) When H_2S is passed through the solution of mercuric salt, a precipitate, insoluble in yellow ammonium sulphide, as well as in 50% nitric acid, is obtained.

(ii) The addition of stannous chloride produces first a white precipitate of mercurous chloride.

(iii) The addition of potassium iodide solution gives a reddish precipitate soluble in excess of potassium iodide.

QUESTIONS

1. How is mercury obtained? How is it refined? Give its properties and uses.
2. Describe in details how pure mercury is obtained from cinnabar. How does it react with (i) chlorine (ii) sulphuric acid and (iii) nitric acid? Mention its important uses.
3. How will you prepare a pure sample of mercuric chloride? Discuss the reactions of mercuric chloride with ammonia and potassium iodide.
4. Describe the preparation, properties and uses of calomel.

CHAPTER XIV (C)

TIN

History. Tin and its various alloys have been known since ancient times. Homer has mentioned this metal as *kassiteros*. The similarity between Greek word *kassiteros* and Sanskrit word '*castira*' has been used as an argument in favour of the eastern origin of the metal. Romans called it 'stannum' from which the modern symbol, Sn, has been derived.

Occurrence. Tin does not occur free in nature. Its chief source is the ore *cassiterite*, SnO_2 , also known as *tin stone*. It also exists along with the pyrite ores of copper, iron and zinc but is rarely extracted out of them.

Extraction. The extraction of tin metal from cassiterite (SnO_2) is conducted through the following stages :

Concentration. Tin stone contains from 0.5 to 10 per cent of SnO_2 . The rest is worthless gangue material. It also contains wolfram which is an isomorphous mixture of ferrous and manganous tungstates, iron pyrites, etc.

Tin stones are crushed and powdered. The worthless gangue material is separated by washing in a stream of water. The heavier ore particles settle to the bottom while the lighter silicious material is washed away. Wolfram, however, has the same density as tin stone and hence cannot be removed by gravity. Its separation is done by electromagnetic means.

The electromagnetic separator is shown in Fig. 14.(C)1. It consists of a travelling belt moving over rollers one of which is electromagnetic. The powdered ore is dropped over the travelling belt. The wolfram being magnetic, falls in a separate heap near to the magnet while the stannic oxide remains undeflected and collects in a different heap, a little farther off.

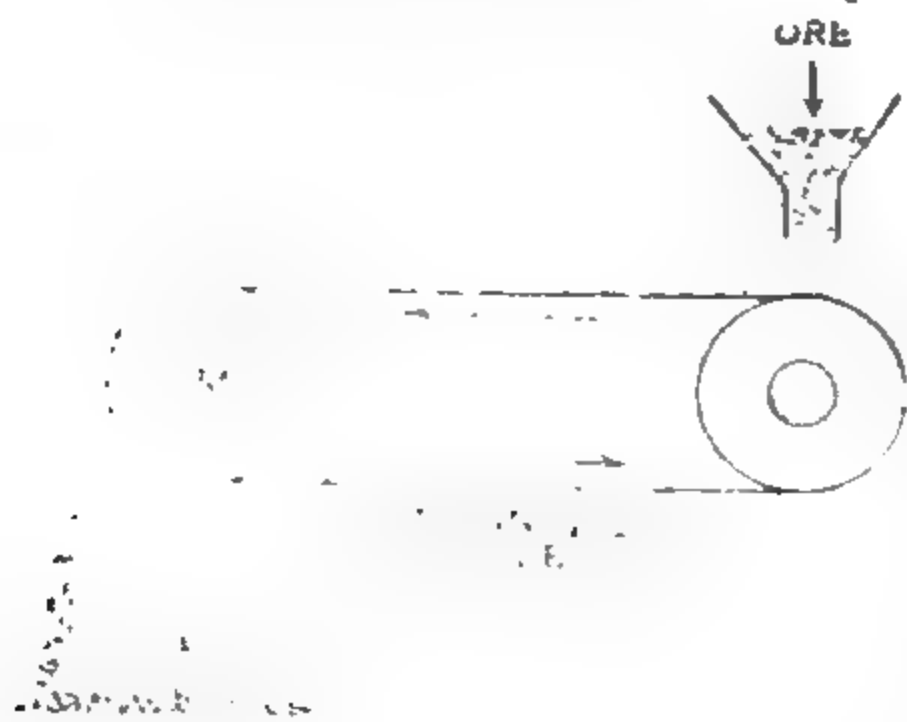


Fig. 14.(C)1. Magnetic separator.

Roasting. The concentrated ore is roasted in a large rotary furnace which is slowly heated in the beginning in free access of air to oxidise sulphur to sulphur dioxide and arsenic to arsenious oxide, which volatilises off.

Smelting. The roasted ore is mixed with anthracite in the ratio of 1 : 4 and subjected to heat in a reverberatory furnace when tin oxide is reduced to the metal.



A small amount of lime is also added as a flux which removes the silica (SiO_2) present as calcium silicate slag. The molten metal is tapped out of the furnace.

Refining. Tin obtained from the reverberatory furnace is crude and contains iron, sulphur, arsenic and tungsten as chief impurities. Its refining is done in two stages :

(i) *Liquation.* It consists in heating the crude tin metal on the sloping hearth of a reverberatory furnace (Fig. 14 (C)2. On account of its low melting point, tin melts earlier and flows down while iron and tungsten along with some tin are left behind. Arsenic and sulphur burn and volatilize off as oxides. The tin thus obtained still retains some impurities and is called *pig tin*. The process is again repeated in another similar reverberatory furnace when pure tin melts more readily at 232°C , and flows down the hearth and is collected in a cast iron vessel.

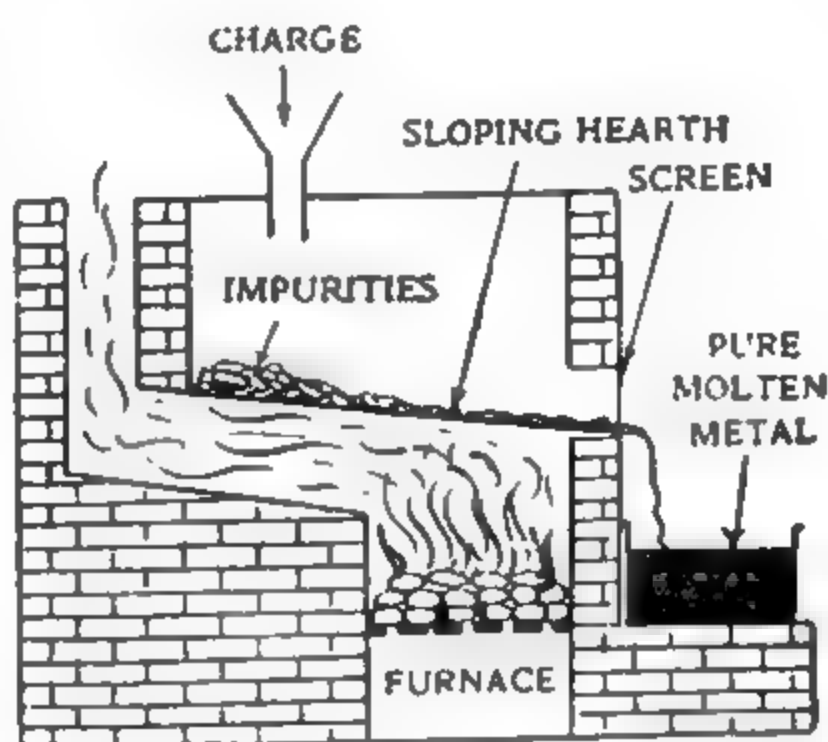


Fig. 14(C)2. Liquation process.

(ii) *Poling.* Further purification is brought about by poling. For this purpose the molten metal is taken in a big pot stirred by green logs of wood. Any tin oxide left unreduced is now reduced by the hydrocarbons of the wood.

Properties of Tin. Physical Properties. (1) Tin has a silvery white lustre which does not tarnish on exposure to air.

(2) Tin exists in three allotropic forms : *grey, white, rhombic*. The transition temperatures are as below :



The densities of the three forms are 5.74, 7.32 and 6.55 respectively. White tin is not only the heaviest but also the most stable variety.

The conversion of white tin into grey tin at 18° , the transition temperature, is exceedingly slow. However, if the temperature is as low as -50° , and a small amount of grey tin is already present, the conversion becomes very rapid. This conversion is known as **tin pest** or **tin disease**.

3. White tin is malleable but not ductile. It becomes brittle when heated at 200° .

4. When bent, the metal produces a cracking noise which is called **tin cry**. This is due to rubbing of crystals over one another.

5. The metal melts at a relatively low temperature of 232° , but boils at a relatively high temperature of 2260° .

Chemical Properties. (1) **Action of air.** At ordinary temperature air has no action on tin but when heated to whiteness ($1500\text{--}1600^{\circ}$) in the presence of oxygen it burns with a bright flame giving stannic oxide.



(2) **Action of halogens and sulphur.** If the metal is heated in the atmosphere of chlorine or sulphur vapour, it readily combines to form stannic chloride and sulphide respectively.



(3) **Action of acids.** Tin is slowly attacked by dilute hydrochloric acid but the reaction becomes rapid on heating with concentrated hydrochloric acid forming stannous chloride and evolving hydrogen.



Dilute sulphuric acid has no action but hot concentrated acid dissolves the metal forming stannous sulphate and evolving sulphur dioxide.



Dilute nitric acid attacks the metal forming stannous nitrate and ammonium nitrate.



Hot concentrated nitric acid produces copious fumes of nitrogen dioxide and metastannic acid.



Organic acids have no action.

(4) **Action of alkalis.** When the metal is heated with alkali solutions it reacts to evolve hydrogen and to form stannites which change into stannates on oxidation by atmospheric oxygen



Uses. (1) Tin is used in the preparation of a number of alloys such as solder, britannia metal, white metal, etc. The names, composition and uses of tin alloys are given in Table 14(C).1.

TABLE 14(C).1

Tin Alloys

Name	Percentage composition	Uses
Solder	Sn 67% Pb 33%	soldering.
Pewter	Sn 75% Pb 25%	making cups, mugs and other utensils.
Babbitt metal	Sn 90% Sb 7% Cu 3%	For bearings and machinery
Britannia metal	Sn 90% Sb 8% Cu 2%	For making table wares
White metal	Sn 82% Sb 12% Cu 6%	For making table wares
Bell metal	Sn 22% Cu 78%	For making bells, gongs, etc.
Rose metal	Sn 2% Pb 48% Bi 50%	For electric fuses.

(2) It is used in the preparation of collapsible tubes for tooth pastes and various ointments.

(3) The metal is extensively used in **tinning** brass utensils. The vessel to be tinned is perfectly cleaned and heated. A pinch of ammonium chloride is sprinkled to remove the oxide film. A small amount of the metal is then fused on the clean surface and rubbed over with the help of a cotton rug until a uniform layer of tin is formed on the surface. To avoid the formation of any oxide which dulls the lustre, the vessel is immediately dipped in cold water.

(4) It is largely used in forming a protective coating over iron. The process is known as **tin plating**. It consists in dipping the clean sheets of iron or steel in a bath of molten tin and then passing through hot pairs of rollers. A thin coherent film of tin is deposited. Such tin plates are used in the manufacture of tin cans, kerosene oil containers and other similar articles.

(5) Tin amalgam is used in making mirrors.

(6) Tin foil is used for wrapping cigarettes and other articles.

Tests for Tin Compounds. When a tin compound is heated in a charcoal cavity it leaves a metallic bead with an incrustation which is yellow when hot and white when cold.

Stannous compounds.

(i) When hydrogen sulphide is passed through a solution of a stannous salt, a *brown* precipitate of stannous sulphide is formed which is soluble in yellow ammonium sulphide.

(ii) Mercuric chloride is reduced first to a white precipitate of mercurous chloride and then to metallic mercury.

Stannic compounds.

(i) When hydrogen sulphide is passed through a solution of a stannic salt, a yellow precipitate of stannic sulphide is formed. It is soluble in yellow as well as in ordinary ammonium sulphide.

(ii) Mercuric chloride does not give any precipitate.

QUESTIONS

1. How does tin occur in nature? How is it extracted from tin stone? Describe the action of the following on tin :

(1) Nitric acid (2) Sulphuric acid (3) Sodium hydroxide (4) Chlorine

2. Name the various allotropic forms of tin. Describe the action of (i) Nitric acid (ii) Hydrochloric acid (iii) Sulphuric acid and (iv) Sodium hydroxide on tin.

3. In what two forms tin occurs and what condition determines their stability? How would you obtain from tin : (a) stannic oxide (b) stannous oxide. In what respects these two compounds resemble and differ from the corresponding compounds of lead?
(Panjab Inter 1960)

CHAPTER XIV (D)

ALUMINIUM

Occurrence. Next to silica and oxygen, aluminium is the most widely distributed element. It is present to the extent of 7.3 per cent in the earth's crust. It occurs :

(i) As impure oxide, commonly known as alumina, Al_2O_3 , in corundum, ruby and sapphire. As hydrated alumina it is present in diaspore, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.

(ii) As silicates in crystalline rock, like felspar, clay (kaolin), mica and slate etc.

(iii) As fluoride in the form of cryolite Na_3AlF_6 ($3\text{NaF} \cdot \text{AlF}_3$).

Extraction. Aluminium was first isolated by F. Wohler in 1847 by heating anhydrous aluminium chloride with potassium. Bunsen (1854) and Deville (1854) prepared the metal (i) by the electrolysis of fused NaAlCl_4 and (ii) by heating NaAlCl_4 with sodium.



However, these methods were very expensive. The modern methods for the cheap production of aluminium are due to Heroult and Hall. Bauxite is the chief ore used in these methods. The process involves the following steps :

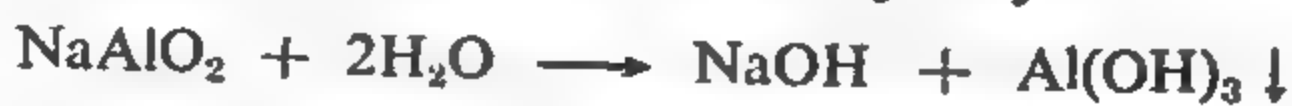
(1) **Purification of Bauxite.** Bauxite usually contains oxides of iron, titanium and silicon as impurities. The first step in the production of aluminium involves the removal of such impurities by one of the following processes :

(a) **Baeyer's process.** Bauxite is ground and digested with sodium hydroxide solution (density 1.45) in an autoclave under pressure at 130° for several hours when alumina present in the ore dissolves as sodium aluminate,



whereas ferric oxide, silica etc., being insoluble, settle down and are

removed by filtration. The sodium aluminate solution is agitated with freshly precipitated $\text{Al}(\text{OH})_3$ for 36 hours when sodium aluminate changes to aluminium hydroxide due to hydrolysis.



Aluminium hydroxide is filtered off, washed and ignited. The filtrate containing sodium hydroxide is concentrated till it again acquires 1.45 density and is used again.

(b) **Serpek's process.** This process is used when bauxite contains relatively a large amount of silica as an impurity. The process has one distinct advantage that it involves the formation of ammonia as a valuable by-product.

Bauxite is heated with carbon at 1800° in a current of nitrogen when aluminium nitride is formed,



which is subsequently decomposed by water.



(c) **Hall's process.** Bauxite is heated to bright redness with sodium carbonate when alumina, being amphoteric in character, dissolves to form sodium meta-aluminate, which is then extracted with water; silica and iron oxide are left as residue.



Carbon dioxide is passed through the sodium meta-aluminate solution when aluminium hydroxide is precipitated.



The solution containing sodium carbonate is concentrated and used again.

Aluminium hydroxide formed by any of the above methods is ignited at 1500° to get alumina.



(2) **Electrolytic Reduction of Alumina.** Pure alumina is reduced to metallic aluminium by electrolysis in fused cryolite between carbon electrodes in a large electrolytic cell. The cell consists of an iron box, measuring $6' \times 3' \times 3'$ (Fig. 14(D).1) It is lined with a refractory material. Within this lining is built a layer of carbon which acts as cathode. A set of carbon rods act as anodes which are movable and can be suspended, raised and lowered, as desired.

The electrolyte is a solution of alumina in fused *cryolite* Na_3AlF_6 . The anodes are immersed in the bath at the desired depth.

The temperature of the bath is maintained at $875-953^\circ$. During the electrolysis, oxygen from alumina reacts with carbon to give

carbon monoxide and carbon dioxide. The relative proportion of the

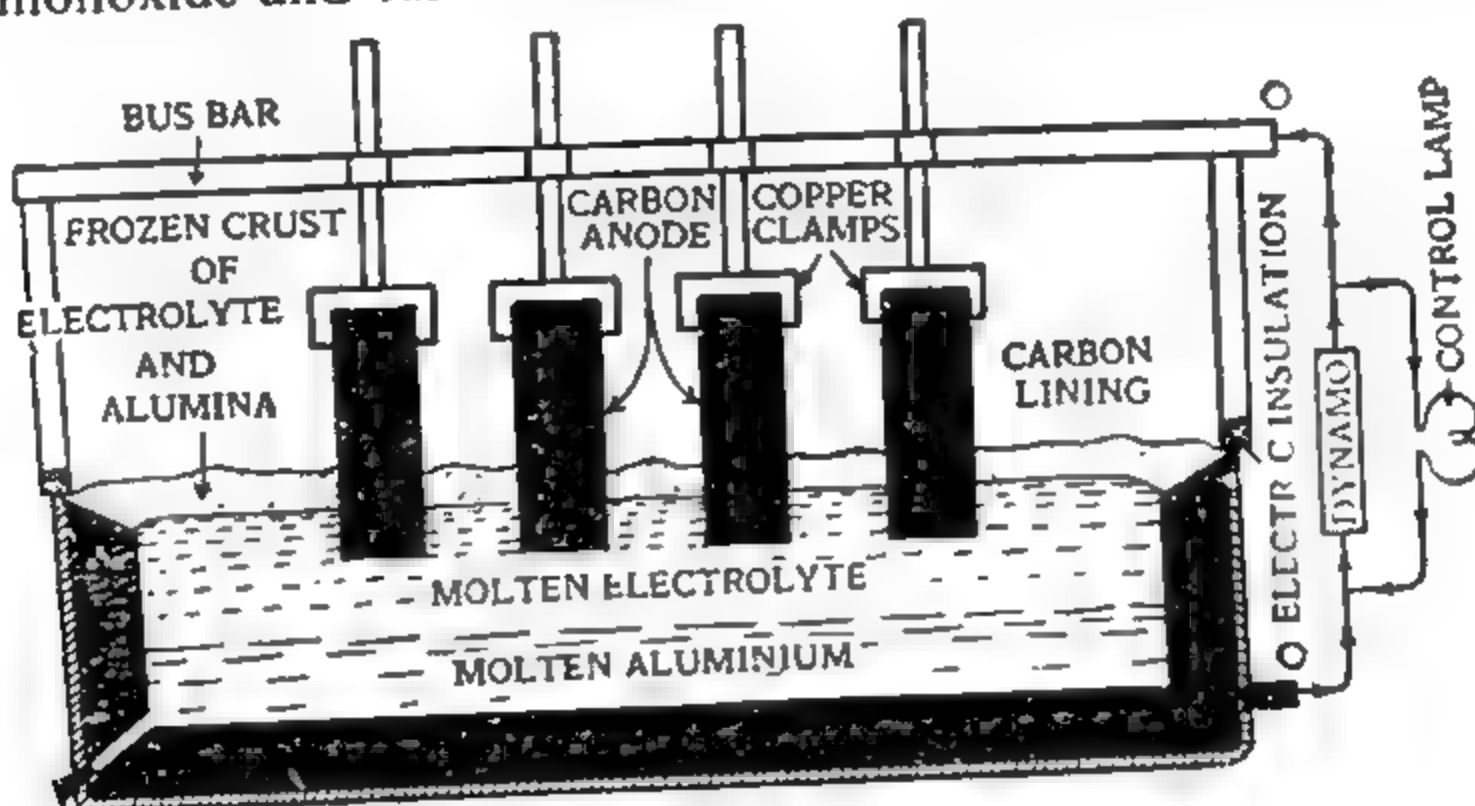


Fig. 14(D).1. Electrolysis of alumina.

two gases in the gaseous mixture depends upon the temperature of the bath. Aluminium is deposited at the cathode along the bottom of the bath and is tapped off from time to time.

The charge is covered with a layer of powdered coke to avoid heat losses by radiation.

When alumina has been exhausted, the resistance of the cell increases and, therefore, more current flows through the control lamp which is connected in parallel with the cell and lights it up. This indicates that more charge (alumina) should be added.

Refining of Aluminium. It is done electrolytically by *Hoope's process*. The refining cell consists of three fused layers :

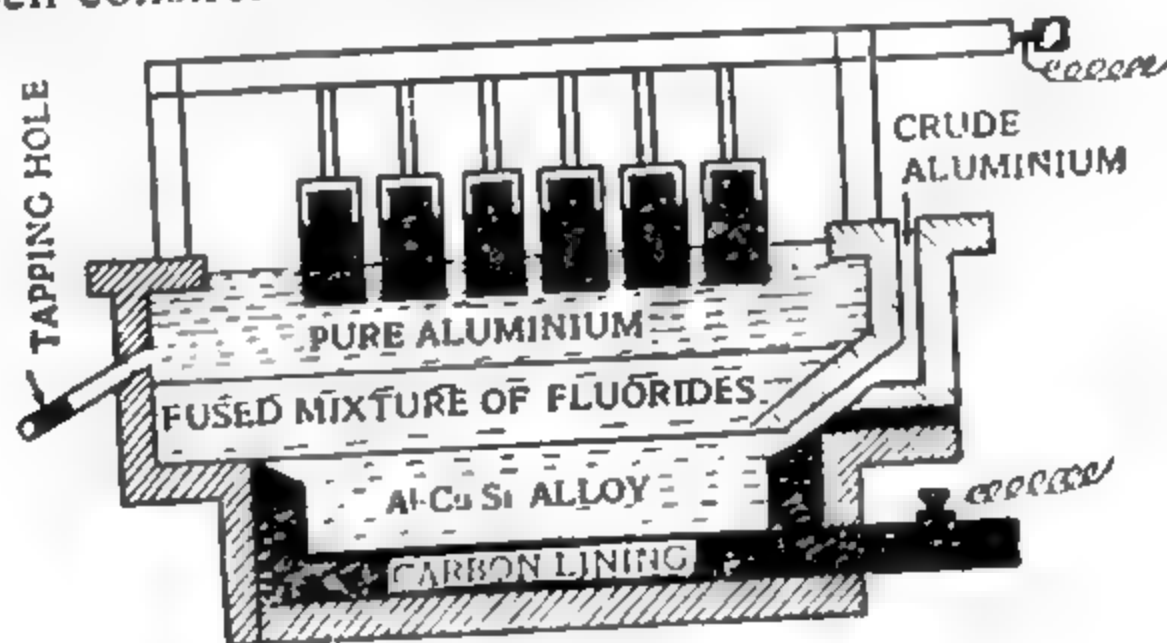


Fig. 14(D) 2. Purification of aluminium

(i) The bottom anode layer of the alloy of aluminium, copper and silicon (ii) the middle layer of cryolite and barium fluoride and (iii) the top cathode layer of the pure metal. The cell is made of iron box lined with carbon. The cell and the various layers are shown in Fig. 14(D).2.

When the current flows, aluminium ions from the fused mixture are discharged at the cathode as pure aluminium which rises to the surface. At the same time an equivalent amount of aluminium from the alloy goes into solution in the middle layer containing the electrolyte. The impurities of copper, etc., remain below.

Physical Properties. Aluminium is a bluish white metal having a brilliant lustre which, however, is soon destroyed due to the formation of an oxide layer. It is malleable and ductile and can be rolled into sheets, foil and wire. It is a very light metal (sp. gr. 2.7). It is a good conductor of heat and electricity. It melts at 659° and boils at 1800° .

Chemical Properties (1) **Action of air.** Aluminium is not affected by pure dry air but in moist air a film of oxide is formed at the surface, which protects the metal from further corrosion. It burns readily in oxygen giving a brilliant light.



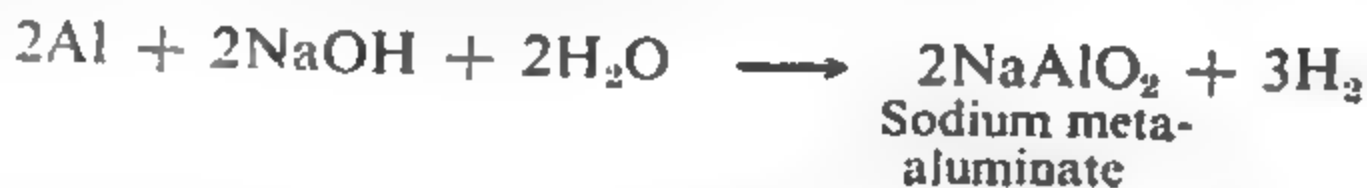
The heat evolved in the oxidation of aluminium is used in the *thermite process* for the reduction of oxides of chromium, iron, manganese, etc.

(2) **Action of water.** Pure aluminium is not affected by pure water. However, the impure form is readily corroded by water containing salts. It decomposes boiling water evolving hydrogen.



Aluminium-mercury couple is, therefore, used as a reducing agent.

(3) **Action of alkalis.** Aluminium readily dissolves in alkalis such as sodium and potassium hydroxides evolving hydrogen and forming the corresponding aluminates.



It also dissolves in a hot concentrated solution of sodium carbonate.



(4) **Action of acids.** Aluminium dissolves in dilute hydrochloric and sulphuric acids evolving hydrogen :



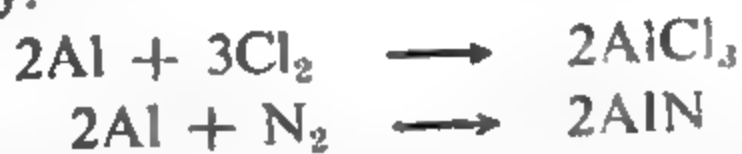
With hot concentrated sulphuric acid, sulphur dioxide is given out.



Concentrated nitric acid has no action.

Organic acids have little action on aluminium at ordinary temperatures but have an appreciable solvent effect in the presence of sodium chloride.

(5) **Action of halogens and nitrogen.** Aluminium when heated with halogens and with nitrogen gives aluminium halides and aluminium nitride respectively.



(6) **Displacement of other metals** Aluminium displaces copper, zinc and lead from the solutions of their salts, e.g.,



Uses. (1) Aluminium, being very light, is used in household utensils, aeroplane parts, precision and surgical instruments, etc.

(2) Since it is unattacked by nitric acid, it is used in chemical plants and also for transporting nitric acid.

(3) Mixed with oil, it is used in paints for steam pipes and other metal objects.

(4) Aluminium foil is used for packing chocolates, cigarettes, etc.

(5) Alums are used as mordants in dyeing and paints.

(6) It is used as a reducing agent for the production of certain metals such as chromium, iron, manganese, etc.

(7) Alumina is used in refractory bricks and ultramarine.

(8) In certain forms such as felspar and mica, it is used in the construction of buildings.

(9) Along with organic colloids, it is used for sizing of paper.

Thermite Welding. The evolution of enormous quantities of heat in the oxidation of aluminium is used in *thermite welding* of metals. This process is also known as *Goldschmidt's aluminothermic process*.

A mixture containing 3 parts of ferric oxide and one part of aluminium powder is placed in a crucible lined with magnesite and having a plug hole (Fig. 14(D).3). This is covered with a layer of a mixture of magnesium powder and barium peroxide, with a magnesium ribbon inserted into it to act as a fuse. The broken ends of a rail or a girder, etc., are brought nearer and thoroughly cleaned and surrounded by a fire-clay mould. When the magnesium ribbon fuse is ignited, the reaction



starts producing a tremendous amount of heat as a result of which the iron melts. This white hot molten iron is tapped from the crucible into the mould. The heated ends of the iron rods (to be welded) actually melt and mix with the molten metal added, giving a firm and strong weld.

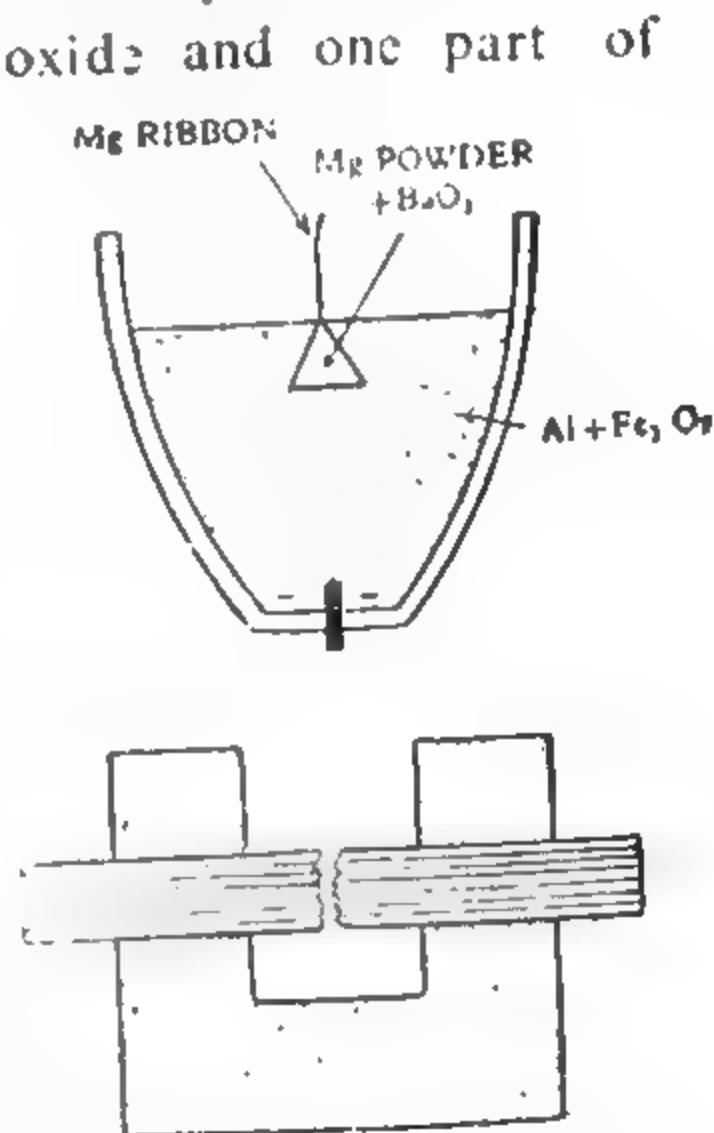


Fig. 14.(D).3. Thermite welding

Potash Alum. $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. It occurs native as a result of the weathering of iron pyrites and alkali rocks. It is manufactured from *alum shale* which contains aluminium silicates and iron sulphide, FeS_2 . It is first roasted when iron sulphide is converted into sulphuric acid which ultimately forms aluminium sulphate.



The clear supernatant liquid is concentrated; the iron salts being less soluble, settle down. To the solution is then added a calculated quantity of potassium sulphate and the mixture crystallised.



Potash alum is also manufactured from *alunite* or *alumstone* $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$. It is calcined and treated with sulphuric acid when the aluminium hydroxide part changes into aluminium sulphate. A little more of potassium sulphate in calculated amount is added and the alum crystallised out.

It is also prepared by crystallising a hot concentrated solution of aluminium and potassium sulphates.

Potash alum melts at 92° and loses all the water of crystallisation when heated at $200^\circ C$.

Potash alum is used as a mordant in dyeing and also for the purification of muddy water.

Tests for Aluminium Compounds.

1. When an aluminium compound is heated in a charcoal cavity, a white residue is obtained. On moistening it with aqueous cobalt nitrate and heating again a blue product, cobalt aluminate, is obtained.

2. When ammonium hydroxide is added to an aluminium salt in the presence of ammonium chloride, a white gelatinous precipitate of aluminium hydroxide is obtained.

3. The addition of sodium hydroxide to an aluminium salt gives a white gelatinous precipitate but it dissolves in excess of the alkali.

4. The addition of ammonium hydroxide to the solution of an aluminium salt in the presence of alizarin gives a pink 'lake like' precipitate.

QUESTIONS

1. What are the important ores of aluminium? Describe how aluminium is obtained from bauxite.

2. How is bauxite purified? Describe how pure aluminium is obtained from the ore. Discuss the action of hydrochloric acid, nitric acid and sodium hydroxide on aluminium.

3. How is aluminium extracted from its ores? Discuss its important uses.

4. Write short notes on:

- Thermite welding
- Purification of aluminium
- Purification of red bauxite.

5. Describe the preparation, properties and uses of potash alum.

6. Describe the extraction of pure aluminium from bauxite. Explain the reactions involved in the process. Write a brief note on aluminothermy.

(Jammu & Kashmir T.D.C. (I) 1966)

CHAPTER XIV (E)

IRON

History. Iron is one of the seven elements (the others being gold, silver, copper, mercury, lead and tin) known since ancient times. It has been used by man in small amounts for centuries but it is only in comparatively recent years that it has gained such importance in the world economy. The alchemists represented iron by the spear and shield (♄), symbol of Mars which they regarded as the god of war. Although it does not occur free in nature, it can be easily recovered from its compounds on reduction with carbon.

The processes of extraction of iron are supposed to have originated in the far East in the prehistoric times. The Romans are reported to have developed the industry in Spain. The modern methods had their beginnings in Germany, about the middle of the fourteenth century, when blast furnaces were introduced, and later, in the early sixteenth century, spread to England. Iron and steel industry was first started in India in Jamshedpur (Bihar) which soon developed into a big industrial concern known as the Tata Iron and Steel Company, Ltd. The production of iron by the Indian Iron and Steel Company, Ltd., after some years, was taken up at Hirapur (Bengal). At present there are three more plants, all in public sector, under the care of the Ministry of Iron and Steel in the Government of India, each having a capacity of over a million tons of steel at Durgapur (Bengal), Bhilai (M.P.) and Rourkela (Bihar). Still another project known as Bokaro (Bengal) is in the offing.

Occurrence. Iron occurs seldom in native (uncombined) form. Some ballistic rocks are said to contain it in small quantities. Many meteorites contain free iron alloyed with 2 to 5 per cent nickel. Iron compounds are essential constituents of living matter. They are present in haemoglobin of blood and chlorophyll of plants.

The most important ores of iron are the oxides, carbonates and sulphides, listed below :

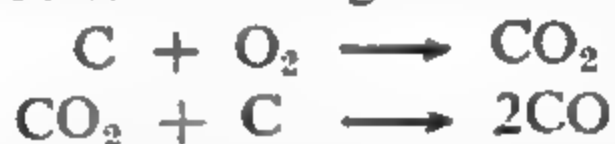
- | | |
|---|--|
| (1) <i>Haematite</i> , Fe_2O_3 | (2) <i>Limonite</i> , $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ |
| (3) <i>Magnetite</i> or magnetic oxide of iron, Fe_3O_4 | |
| (4) <i>Siderite</i> or spathic iron ore, FeCO_3 | (5) <i>Iron pyrites</i> , FeS_2 |

Iron pyrites occur abundantly but actually it is not a source of iron. It is used mostly as a source of sulphur for the manufacture of sulphuric acid.

Varieties of Iron. There are three main varieties of iron which are put to different industrial uses. The difference in their properties lies in the difference in their carbon and phosphorus contents. Wrought iron is the purest form. Cast iron is the least pure and contains 2.5 to 4.5 per cent of carbon along with some sulphur, phosphorus, silicon and manganese.

The manufacture of cast iron will be described first as it is this variety from which the other two commercial forms are prepared.

Metallurgy. The Principle. Iron is extracted chiefly from its oxide ore by heating in the presence of coke and limestone. At first the burning coke combines with oxygen to form carbon dioxide which reacts with more hot carbon to give carbon monoxide.



This carbon monoxide then reacts with the ferric oxide contained in the ore giving iron and carbon dioxide.



Silica and other such constituents in the ore are removed as calcium silicate slag on reacting with calcium oxide which results from the heating of lime stone.



The Process The process involves the following stages :

(i) **Concentration of the ore.** The oxide (generally haematite) ore is split into pieces about 1 inch in size and then washed with water to remove clay, sand, etc.

(ii) **Calcination.** The ore is then calcined (heated strongly in the presence of air) to remove water as well as to decompose carbonates and to burn off sulphur and arsenic, if any.

(iii) **Smelting. Blast Furnace.** The calcined ore is then smelted, i.e., reduced with carbon in the presence of a flux to remove silicon impurities. This is done in a **blast furnace** shown in Fig. 14(E).1. It is a steel structure lined with firebricks, 100 feet high and 25 feet in diameter at its widest part. It is slightly narrow at the top and again at the bottom. This facilitates a proper flow of the materials.

The furnace at its base is provided with (i) small pipes called *tuyeres* (A) through which hot air is admitted, (ii) a *tapping hole* (B) through which molten iron can be withdrawn and a *slag hole* (C), through which slag flows out. At the top, the furnace carries a hopper (H), which rests over a *cup and cone* arrangement. This prevents the exit of gases during the charging of the furnace.

The charge, consisting of the calcined ore mixed with coke and limestone in the approximate ratio of 4 : 2 : 1, is carried to the top of the

furnace and introduced in it by means of the cup and cone arrangement. At the same time the furnace is lit and a blast of hot air is sent upwards through the *tuyeres*. The following reactions take place in the furnace :

(i) The temperature at the bottom of the furnace (close to the *tuyeres*) is sufficiently high to cause the combustion of the coke forming carbon dioxide.

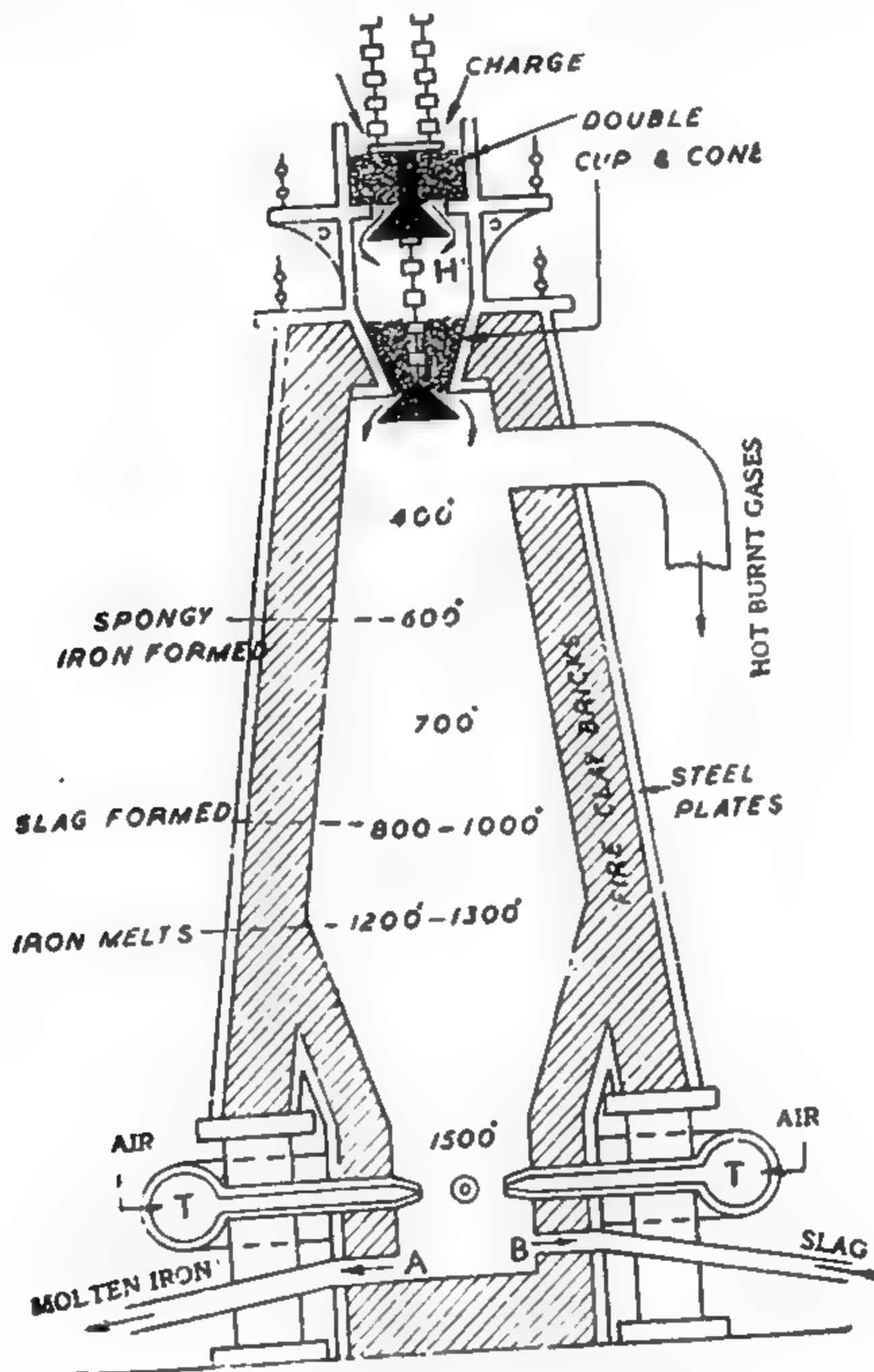


Fig. 14(E).1. Blast furnace.

(ii) As this carbon dioxide rises upwards it comes into contact with the overlying layers of coke at a temperature of above 1500°, and is reduced to form carbon monoxide.



(iii) The reduction of the ore by carbon monoxide starts near the top. First, the ferric oxide is reduced to ferrous oxide at about 600°.



Ferrous oxide is then reduced to metallic iron at about 750° .



Both the above reactions are exothermic, evolving in all 8.5 kilocal. of heat.

Iron produced at the prevailing temperature (750°) is in the solid state. But as it drops down gradually through the hotter portions of the furnace, it melts, dissolves some carbon, phosphorus and silica, and collects at the bottom, as cast iron.

(iv) The limestone decomposes at this point to form carbon dioxide and lime.



The lime combines with the silica of the ore to form a slag of calcium silicate.



The molten slag settles down and, being lighter, forms a separate layer above the molten iron and protects it from oxidation. The two layers can be withdrawn through separate tapping holes *A* and *B*, as shown.

The gas which leaves the furnace at the top contains about 25 per cent of carbon monoxide. It is burnt in special stoves (Cowper's stoves or preheaters) in excess of air. The heat thus produced is used in raising the temperature of the air blast that enters the furnace through the tuyeres, *T*.

The various reactions taking place in the blast furnace are shown in Fig. 14(E).2.

The molten metal withdrawn from the furnace is called pig iron. It contains 2.6–4.3 per cent of carbon and varying amounts of manganese, silicon, sulphur and phosphorus. It is converted into wrought iron or steel, or cast into moulds which on re-melting and re-cooling is called cast iron.

The slag withdrawn from the furnace through the separate tapping hole is put to several

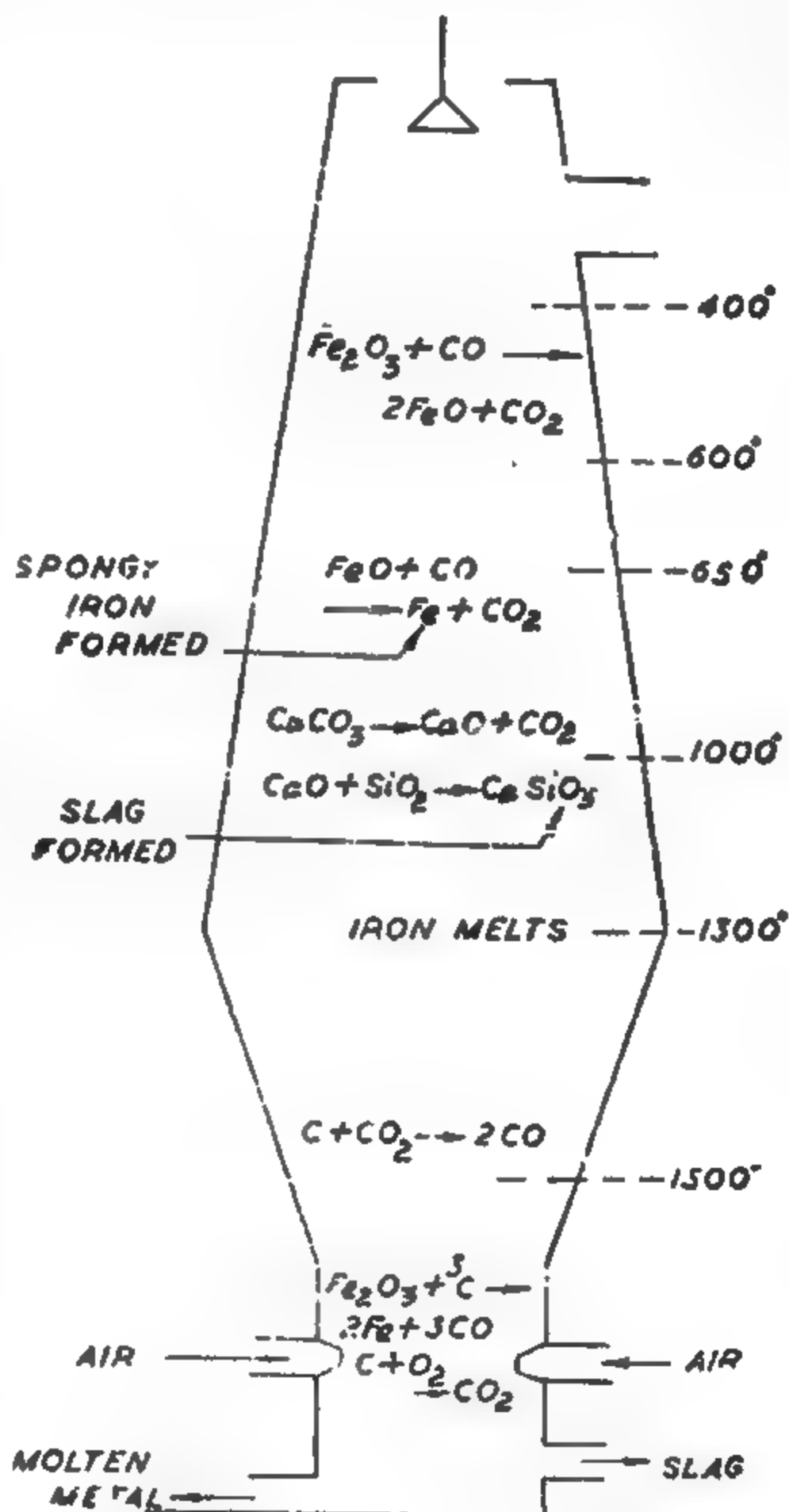


Fig. 14(E).2. Reactions in the Blast furnace.

uses, such as in road building, in production of cement and in the surfacing of railroads.

The operation in the blast furnace is almost continuous. The furnace is charged with about 2400 tons of iron ore, 1200 tons of coke and 600 tons of limestone a day. It would produce about 1200 tons of pig iron and 500 tons of slag every day.

Properties and Uses of Cast Iron. Cast iron contains from 2.5 to 4.5 per cent carbon, 0.7 to 3 per cent silicon and small quantities of phosphorus, sulphur and manganese. The carbon is present partly as free carbon in the form of graphite and partly in combination with iron as *cementite*, Fe_3C . When it is melted and then rapidly cooled, it is very hard and brittle and is known as **white cast iron**. This contains most of the carbon as cementite only. If the molten iron is cooled slowly, on the other hand, most of the carbon separates out as graphite and a softer and less brittle variety known as **grey cast iron** is obtained.

Cast iron, on account of impurities, melts at a much lower temperature of 1150 to 1250° whereas pure iron melts at 1535°.

It is hard but too brittle to be used in making machinery. It expands on solidifying and therefore finds extensive applications in casting variously-shaped articles such as stoves, radiators, toys, stools, cooking ranges, pipes, agricultural implements, etc.

WROUGHT IRON

Wrought iron is comparatively pure form of iron. It contains not more than 0.5 per cent of impurities of which carbon amounts to about 0.2 per cent. The other impurities are sulphur, phosphorus, silicon and manganese.

Manufacture. It is obtained by purifying cast iron by the process known as '**puddling**' (meaning stirring). The cast iron is heated on the

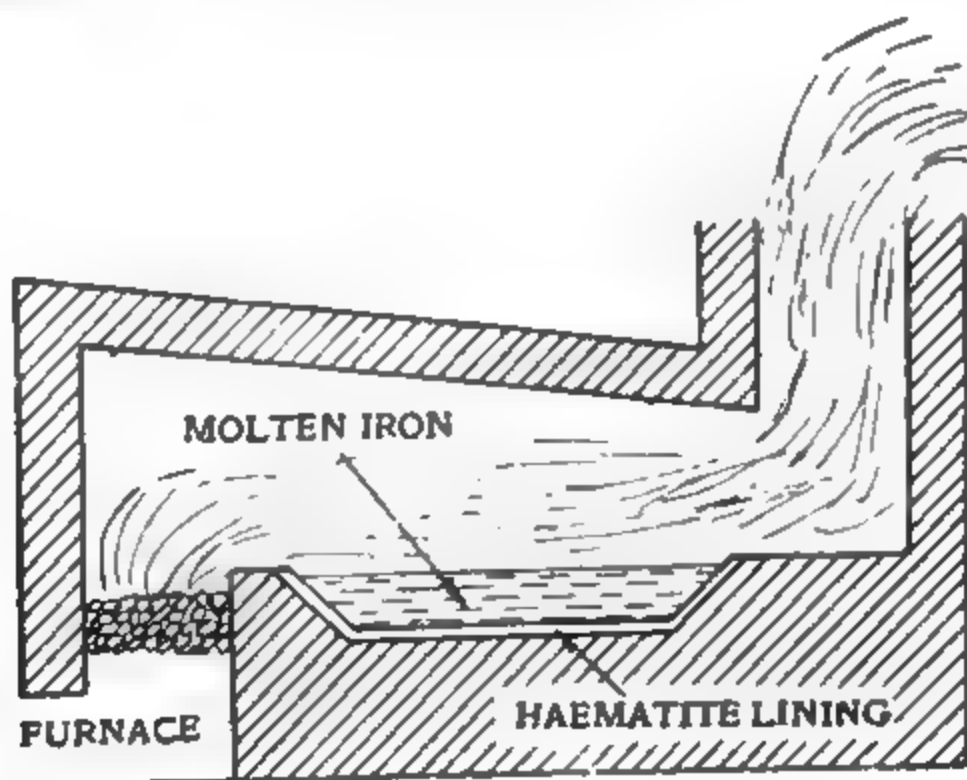


Fig. 14(E).3. Puddling furnace.

hearth of a reverberatory furnace (known as puddling furnace, Fig. 14(E).3) lined with haematite (Fe_2O_3). The pig iron is melted and stirred. The haematite supplies the oxygen required to oxidise the carbon, silicon, manganese and phosphorus present in the cast iron to carbon monoxide,

silica, manganous oxide and phosphorus pentoxide respectively. For example,



Carbon monoxide escapes. Manganous oxide and silica combine to form manganous silicate slag.



Phosphorus pentoxide combines with haematite to form ferric phosphate slag.



The melting point of iron rises with the loss of impurities. Iron, therefore, attains a semi-solid state. At this stage it is taken out in the form of balls and the slag squeezed out by hammering.

Properties and Uses. Wrought iron retains about 0.2 per cent of carbon besides traces of phosphorus, silicon, etc., in the form of slag. It is soft, ductile and malleable and can be welded. The presence of slag gives strength and toughness to the metal and makes it resistant towards rusting and corrosion. It is used in the manufacture of articles which are to be subjected to sudden stresses, such as chains, wires, anchors, bolts, nails. It is also used in making cores of electromagnets.

STEEL

The carbon content of steel is intermediate between that of cast iron and wrought iron. It varies between 0.1 and 1.5 per cent. The hardness of steel increases with increase in carbon content. Steel usually contains manganese as well. Sometimes, other elements such as chromium, silicon, nickel, tungsten, vanadium and molybdenum are added for making special steels.

There are three methods in common use for the production of steel on a large scale. These are (i) the *Bessemer process* (ii) the *Open Hearth Process* and (iii) the *Electric Furnace Process*. They are based on removing impurities from pig iron and then adding calculated amount of carbon, manganese, chromium and other elements.

1. The Bessemer Process. In this process, molten pig iron taken direct from the blast furnace is run into Bessemer converter which is a pear-shaped furnace

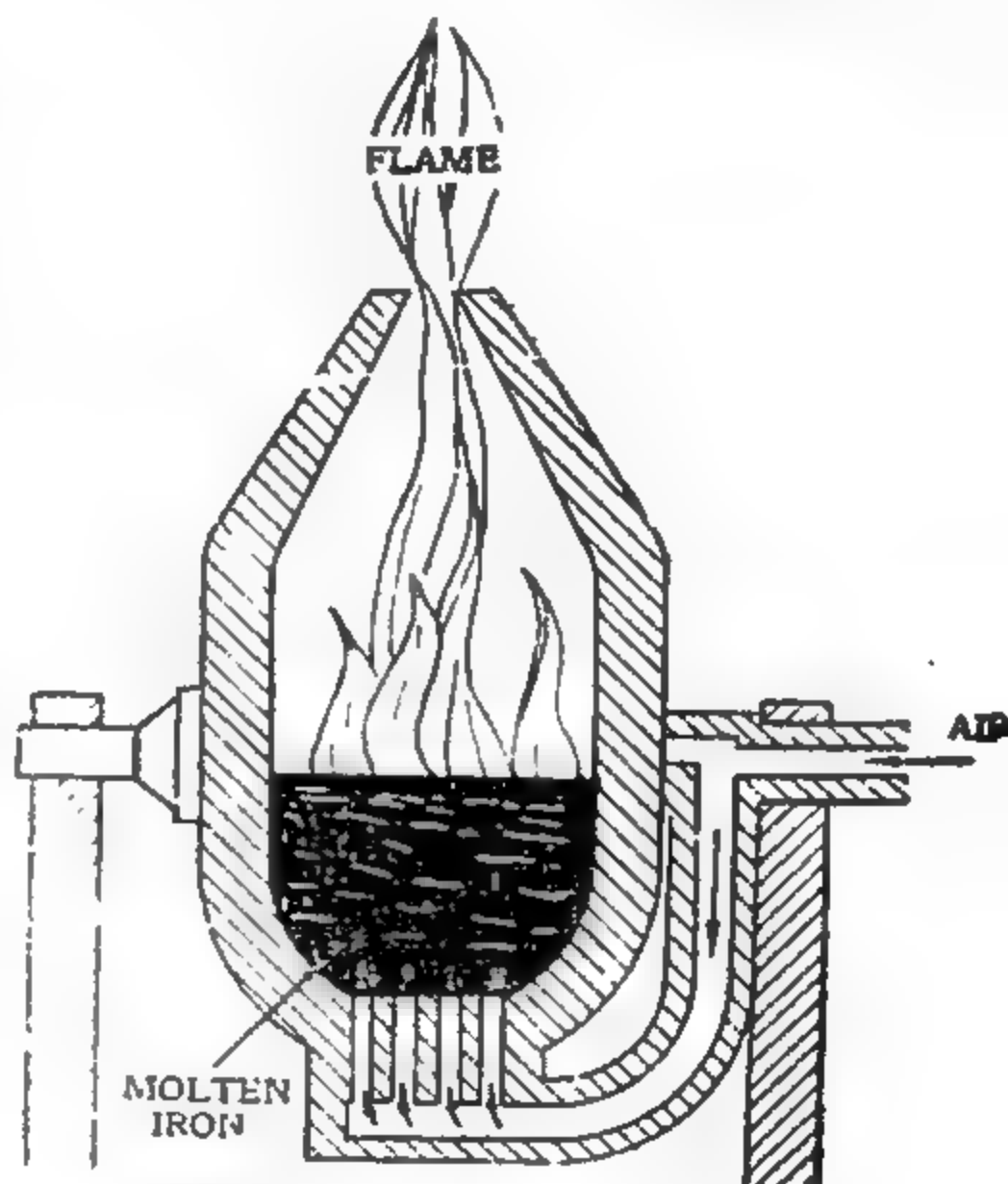


Fig. 14(E).4. Bessemer converter.

about 20 feet high and 10 feet in diameter (Fig. 14(E).4). It is made of steel plates and is lined inside with silicon heat-resisting bricks. At the base there are a number of holes called *tuyeres* through which air can be admitted. The converter can be rotated on a horizontal central axis.

To start with, the converter is turned into the horizontal position and molten pig iron introduced into it. A blast of hot air is admitted through the tuyeres. The converter is then rotated so as to bring its mouth vertically upwards. The blowing of air is continued. As the air passes upwards through the molten metal, it oxidises the impurities (manganese, silicon, carbon) present in pig iron.



During the first five to ten minutes, oxidation of only manganese and silicon takes place. The manganese oxide and silica thus formed combine together to form manganous silicate slag.



Later, carbon is oxidised to carbon monoxide which burns with a blue flame at the mouth of the converter.

When the whole of carbon is oxidised the blue flame suddenly dies out. The requisite amount of carbon is then added (to convert iron into steel) usually in the form of an alloy of iron, manganese and carbon, called *spiegeleisen*. The blast is continued just for a moment to ensure complete mixing. The resulting product is **manganese steel**, which is much harder and possesses much greater tensile strength than ordinary steel.

At the end, the converter is tilted to pour out the molten steel.

If cast iron from which steel is to be obtained contains much of phosphorus, the converter is lined with lime (CaO) and magnesia (MgO), instead of silica. Some lime is added to the charge. The phosphorus present is oxidised to phosphorus pentoxide, which forms a slag of calcium phosphate.



The slag, also known as *Thomas slag*, is ground and used as a valuable fertilizer.

2. The Open Hearth Process. In this process a mixture of cast iron, scrap iron, iron ore (haematite) and lime is melted in an Open Hearth furnace (Fig. 14(E).5). The hearth is lined with silica (SiO₂) or calcined dolomite (CaO, MgO) depending upon the nature of the impurities present in cast iron. Silica lining is useful if the impurities are manganese, silicon, etc., and calcined dolomite lining is used if much of phosphorus is present. Heating to about 1500° is done by burning producer gas. A **regenerative**

system of heat economy is employed to save the fuel. This is accomplished by using a set of heat regenerators, made of brick-checker work (cf. Fig. 14(E).5.) Producer gas is led into the regenerator G_1 which has been previously heated. Air is passed through another regenerator G_2 which is also heated. The producer gas burns in the air over the hearth of the furnace producing a tremendous amount of heat which is utilised in melting the charge. The products of combustion leave the furnace through the regenerators G_3 and G_4 passing on their heat to the regenerators. When the latter have been sufficiently heated, the direction of the producer gas and air is reversed. Now the gases, before entering the furnace, pass through the hot regenerators G_3 and G_4 . They pick up the heat of the regenerators and consequently on combustion produce a much greater amount of heat than otherwise.

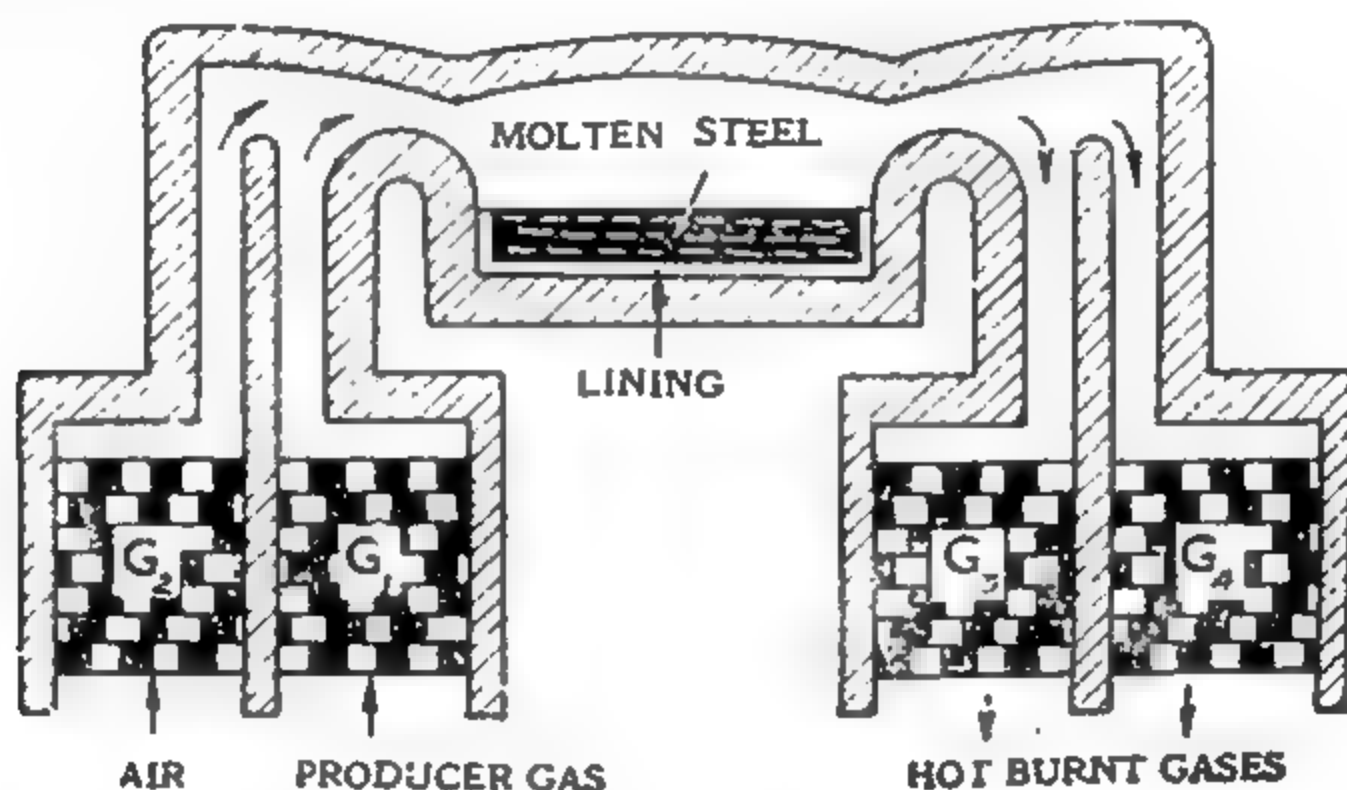
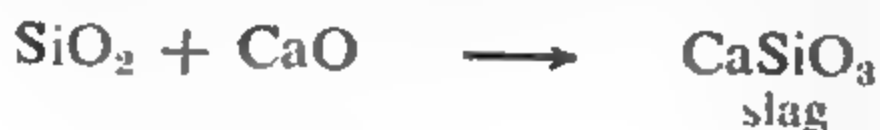


Fig. 14(E).5. The Open Hearth furnace.

The products of combustion now pass through the regenerators G_1 and G_2 which get heated up again. After 10—15 minutes, the supply of producer gas and air is again reversed and so on. In this manner, a considerable amount of fuel is saved.

Heating is continued for about 8 to 10 hours. During this period, the impurities (C, Si, S, P) get oxidised by haematite. Carbon is removed as carbon monoxide. Sulphur is eliminated as sulphur dioxide. Silicon and phosphorus are oxidised to silica (SiO_2) and phosphorus pentoxide respectively. These react with lime forming slag.



Samples are withdrawn from the hearth from time to time and analysed. The carbon content is adjusted to the proper value. Requisite quantities of other metals may also be added if special steels are to be obtained. After setting up the desired composition, the finished batch of molten steel is removed from the furnace by tilting the hearth.

Huge quantities of high grade steel of the desired composition are prepared by the Open Hearth Process.

Advantages of the Open Hearth Process. The Open Hearth Process has the following advantages over the Bessemer Process :

(i) The composition of the product and also the temperature can be accurately controlled.

(ii) Scrap iron and ore can be directly changed into steel.

(iii) No iron is lost as slag since no blast of air is passed through the molten metal.

(iv) A considerable economy of fuel is effected by using the regenerative system of heat economy.

(v) The steel obtained is of a better quality.

3. The Electric Furnace Process. A very high grade steel in relatively small amounts is prepared by the electric furnace process where electric supply is cheap. A mixture of cast iron, scrap iron and iron ore (e.g., haematite) is heated in an electric furnace with dolomite. The reactions taking place in the furnace are essentially the same as in the open hearth process. Since very high temperatures can be developed in electric furnaces, the process becomes particularly useful for preparing alloy steels with high melting points.

Some special alloy steels have been described in the following table :

Name	Composition	Properties	Uses
1. Chrome steel	2.4% Chromium	High tensile strength	Ball bearings, cutting tools such as files.
2. Tungsten steel	10-20% Tungsten	Retains hardness even at high temperatures	Cutting tools for high speed lathes.
3. Stainless steel	18% Chromium 8% Nickel	Resists corrosion	Utensils, ornamental pieces.
4. Manganese steel	10-18% Manganese	Very hard and resistant to wear.	Grinding machinery, safes.
5. Nickel steel	2-4% Nickel	Resists corrosion, hard and elastic	Wire cables, gears, drive shafts.
6. Molybdenum steel	0.3-3% Molybdenum	Retains hardness even at high temperatures	Cutting tools and axles.
7 Invar	36% Nickel	Practically no coefficient of expansion	Meter scales and pendulum rods.

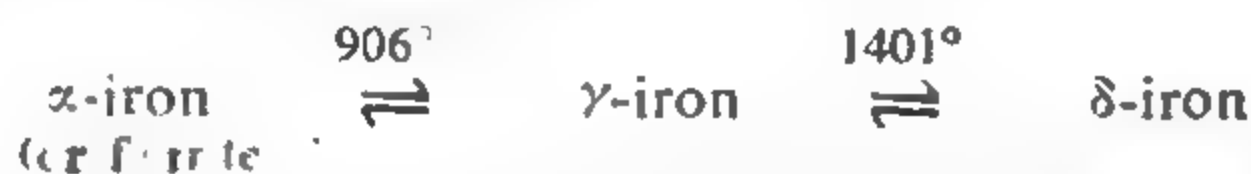
Tempering. Steel has a highly characteristic property that its hardness and elasticity can be controlled by proper heat treatment. For example,

when it is heated to red heat and then allowed to cool *slowly*, it becomes soft. This process is known as **annealing**. On the other hand, if it is cooled (quenched) *suddenly* on plunging into ice-cold water, it becomes very hard and brittle. On reheating this product to 250—300°, the brittleness disappears but hardness remains. The degree of hardness can be controlled by heating the product once again to a suitable temperature varying from 200 to 350° (depending upon the hardness required) and then allowing it to cool slowly. This process is known as **tempering**. The temperature to which steel is heated is judged from the colour of the oxide film formed on the surface, *e.g.*, a pale yellow colour indicates 230°, brown 260°, purple 225° and blue 300°.

Properties of Pure Iron.

Physical Properties. Pure iron is grey-white in colour. It softens before melting at 1535°. It boils at about 3,000°. Its specific gravity is 7.86 and specific heat 0.11. It possesses strong magnetic properties which it loses when heated above 766° (the *curie point*). It is malleable and ductile but has a very high tensile strength.

The metal exhibits allotropy. It exists in three forms which differ from one another in crystalline shape only. The names and transition temperatures are



The name β -iron is given to the non-magnetic form produced at 766°. However, it has the same crystalline form as α -iron and is, therefore, not considered as a distinct allotropic form.

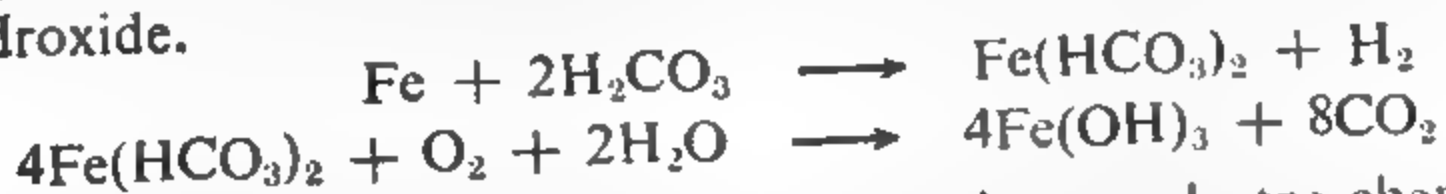
Chemical Properties. Chemically, iron is a fairly active element as will be evident from the following reactions :

1. Action of air. The rusting of iron. It has been known since ages that commercial iron on exposure to moist air gets coated with a 'fuzzy reddish brown deposit' known as **rust**. Although the chemical composition of rust varies some what, it consists mainly of hydrated ferric oxide, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, together with a small quantity of ferrous carbonate. Pure iron if kept in contact with pure (redistilled, CO_2 -free) water, does not rust. The rust appears if iron is impure or if water contains some dissolved impurities.

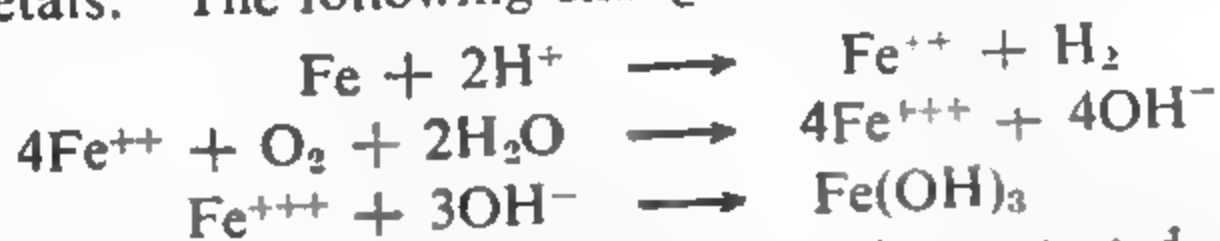
Several workers have carefully investigated the conditions which promote rusting. The results have been somewhat divergent. However, the presence of water is essential and according to many experimenters carbon dioxide or acidity is also necessary. The presence of even traces of other metals, such as zinc or copper in the iron, promotes the formation of rust.

On the other hand, the presence of certain metals which can form solid solutions with iron, such as chromium, nickel and copper, renders the iron rustless. The presence of alkalies, if added to water, also retards rusting.

Theories of rusting. Since carbon dioxide promotes the formation of rust, it has been suggested that ferrous bicarbonate is first formed which is then oxidised by dissolved oxygen with precipitation of ferric hydroxide.



According to another view, rusting is an electro-chemical phenomenon and takes place due to local action. When impure iron comes in contact with water containing carbon dioxide, an internal voltaic cell is set up. The iron and the other metals present as impurities constitute the electrodes while water charged with carbon dioxide acts as an electrolyte. As iron is more electropositive than many other metals, it passes into the acid solution as ferrous iron more readily than the other metals. The following changes are indicated :



Protection of iron from rusting. Iron is protected from rusting by coating with zinc or painting or white-washing with lime. Iron pipes are protected by heating and then dipping into a solution of coal tar. An impervious coating results. Another method, known as *Barf process*, consists in heating the iron to redness in steam when a protective coating of ferrosferric oxide (Fe_3O_4) is formed. The oxide layer is very firm and coherent and can be removed only by heating with water containing magnesium chloride.

(2) **Action of water.** Iron displaces hydrogen from steam at high temperatures.



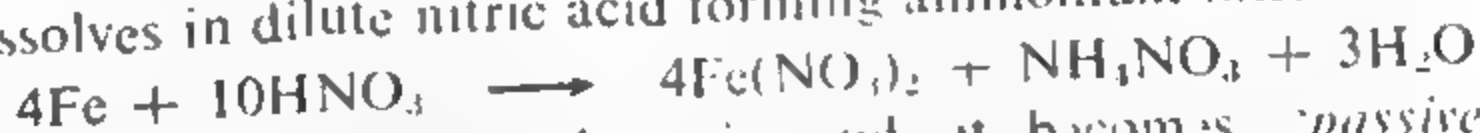
(3) **Displacement of other metals.** Iron displaces less active metals such as copper, silver, etc., from their salts.



(4) **Action of acids.** Iron dissolves in dilute hydrochloric and sulphuric acids liberating hydrogen.

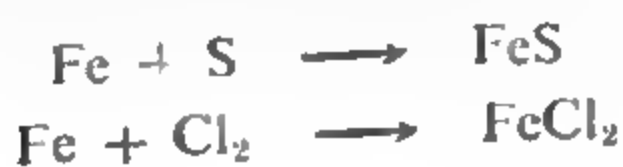


It also dissolves in dilute nitric acid forming ammonium nitrate.



When placed in concentrated nitric acid, it becomes 'passive', i.e., it loses its normal reactivity. For example, it does not dissolve in dilute acids nor displaces copper from solutions of its salts.

(5) **Combination with other elements.** Iron combines directly with sulphur and chlorine forming iron sulphide and iron chloride respectively.



Passive Iron. When a piece of iron is lowered in concentrated nitric acid, a slight reaction takes place and then ceases completely. The iron does not appear to undergo any change in its appearance but it does not react with dilute nitric acid nor does it precipitate copper from copper sulphate although ordinary iron undergoes these reactions very readily. The iron in this form is said to be 'passive'. Iron also becomes passive when dipped in a solution of chloric acid, chromic acid, potassium permanganate or silver nitrate or when treated with dry nitrogen dioxide or subjected to anodic oxidation.

Passive iron returns to the normal state when scratched or heated in a reducing atmosphere of hydrogen or carbon monoxide or immersed in a concentrated solution of an alkali.

Faraday suggested that passivity is due to the formation of an extremely thin (almost imperceptible) and impervious film of ferroso-ferric oxide, Fe_3O_4 . This view receives support from the fact that the passivity is removed by scratching or by dissolving out the iron oxide in iodine solution.

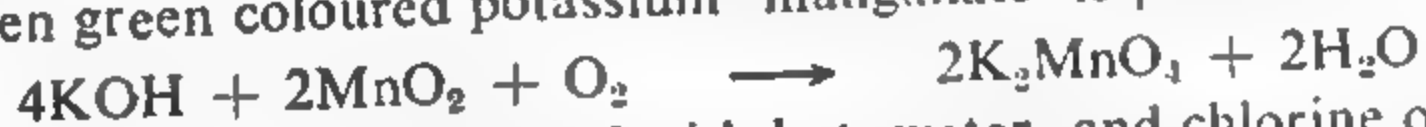
QUESTIONS

1. What are the important ores of iron? How is pig iron obtained from haematite ore?
2. What are the different forms of iron? Summarise with the help of equations the reactions taking place in the blast furnace used in the metallurgy of iron.
(Delhi Pre-medical 1949)
3. Sketch a blast furnace. Label the parts. Describe the reactions taking place in the blast furnace.
4. Describe the extraction of iron from its ore. Give the important properties and uses of cast iron.
5. Give in outline the extraction of iron from ores in India. What precautions, if any, should be taken in the selection of the ore for the purpose? How would you distinguish a sample of cast iron from steel? (Panjab Inter 1960, Rajputana Inter 1952)
6. Describe, giving neat diagram, the manufacture of steel from cast iron. Describe the statement "the properties of steel depend on (a) its carbon content (b) its heat treatment (c) alloy elements".
7. Give one method for the conversion of iron into steel. What is the difference in the composition and properties of (i) cast iron and (ii) steel? How are the properties of iron altered on (i) heat treatment and (ii) addition of other elements?
(Rajputana Inter 1956)
8. Describe in details the Bessemer Process for the conversion of cast iron into steel. What is meant by (i) annealing and (ii) tempering of steel?
9. Describe in details the Open Hearth Process for the preparation of steel. What is meant by a regenerative system of heat economy? What advantages the Open Hearth process possesses over the Bessemer Process?
10. Describe the puddling furnace for the preparation of wrought iron. Discuss important properties and uses of wrought iron.
11. What is steel. Describe the Bessemer Process for the manufacture of steel. Why is steel prepared by this method regarded inferior to steel obtained by the Open Hearth Process? Upon what factors depend the properties of steel?
(Rajputana Inter 1946, U.P. Board 1948)

CHAPTER XV

SOME IMPORTANT COMPOUNDS

Potassium Permanganate. The pyrolusite ore, MnO_2 , is the usual source for the production of potassium permanganate. The ore is finely powdered and then fused with caustic potash in the presence of excess air when green coloured potassium manganate is produced :



The fused mass is extracted with hot water and chlorine or ozone is passed into the solution when potassium manganate is oxidised to potassium permanganate :

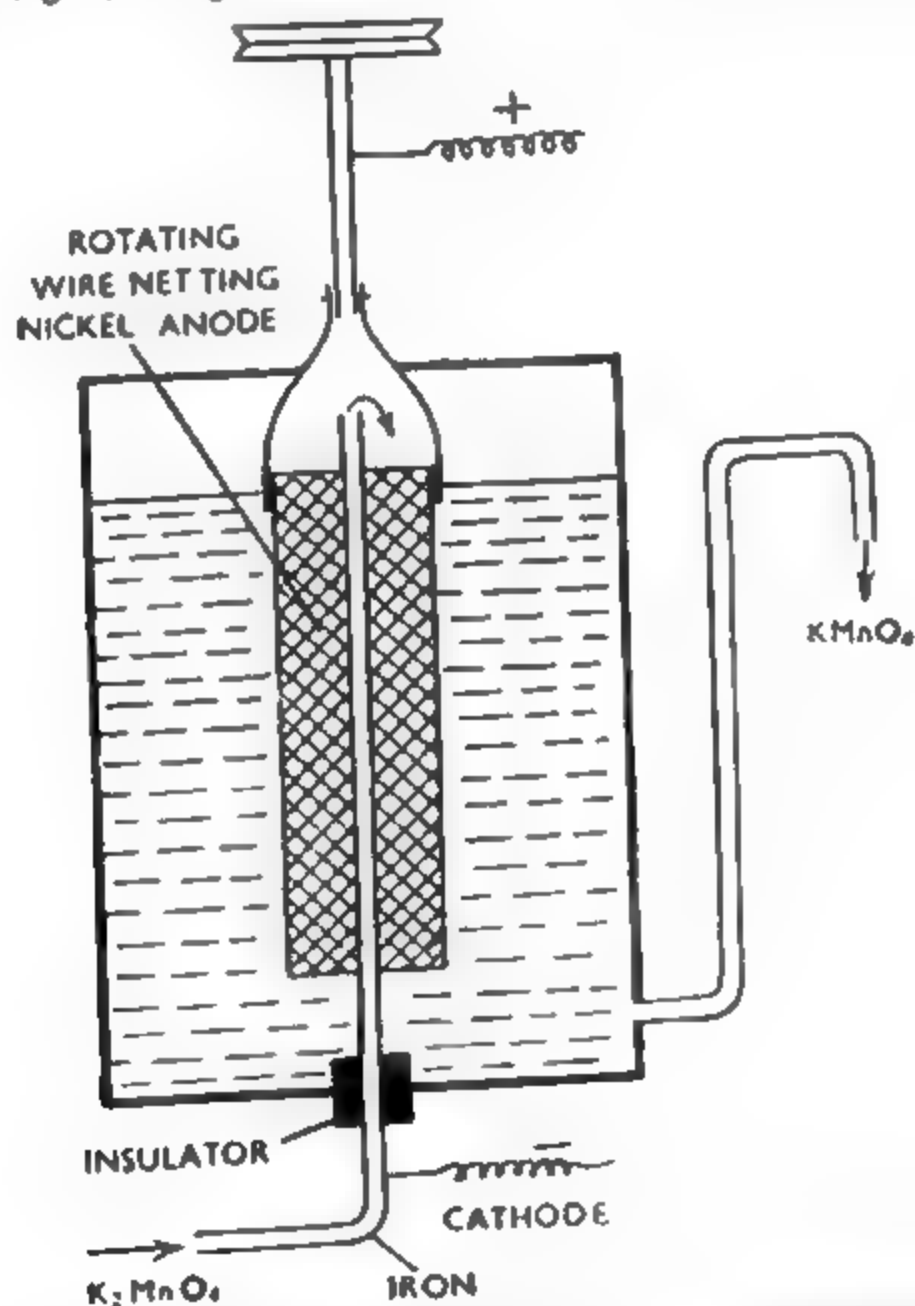


Fig. 15.1. Electrolytic method for the preparation of potassium permanganate.

The solution is concentrated when potassium permanganate, being less soluble, separates out on cooling leaving more soluble potassium chloride in the solution.

Nowadays the conversion of potassium manganate into potassium permanganate on industrial scale is carried out electrolytically using a nickel anode and an iron cathode. The manganate ion is oxidised to permanganate ion by losing an electron in the anode compartment :



The electrolytic cell used for the purpose is shown in Fig. 15.1. The inlet iron pipe, through which the solution of potassium manganate is admitted into the cell is made the cathode while a rotating wire-netting of nickel is made the anode.

Properties. (1) Like all other permanganates, potassium permanganate has the characteristic purple colour. It is soluble in water giving a dark purple solution.

(2) On heating it decomposes :



This reaction is used to prepare oxygen.

(3) When dropped in *cold* concentrated sulphuric acid, manganese heptoxide is obtained :

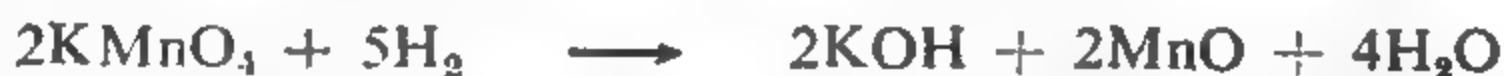


(4) In alkaline solutions, it is reduced to potassium manganate :



(5) Potassium permanganate is a strong oxidising agent in the solid state as well as in neutral, alkaline and acidic solutions.

(a) *In solid state.* When heated in hydrogen, steam is produced :



Hydrochloric acid is oxidised to chlorine :



(b) *In neutral solution.* In neutral solution, potassium permanganate gives dioxide and *three atoms of oxygen become available for oxidation.*



Thus, manganese sulphate, in neutral medium, is oxidised to manganese dioxide :



(iii) *In alkaline solution.* In alkaline solution, potassium permanganate changes into potassium manganate and *one atom of oxygen becomes available for oxidation.*



Potassium manganate is further reduced particularly in the presence of a reducing substance.



Thus, the complete reaction is



It is evident that *the reaction in neutral as well as alkaline solution is the same.*

Thus, in alkaline medium, potassium iodide is oxidised to potassium iodate :



(iv) *In acid solution* In acid solution (dilute sulphuric acid is generally used), manganous salts are formed and 5 atoms of oxygen are rendered available :



Thus, in acid solution ferrous sulphate is converted into ferric sulphate, sulphurous into sulphuric acid, oxalic acid into carbon dioxide, potassium iodide into iodine, ethylene into glycol, ethyl alcohol into acetaldehyde and acetic acid, etc :



Uses. 1. Potassium permanganate is largely used as an oxidising agent.

2. In laboratory, it is used in volumetric estimation of oxalic acid and of iron in the ferrous state. It is also used for the detection of double bond in organic compounds (*cf.* its reaction with ethylene) and of chloride, bromide and iodide and oxalates in inorganic compounds. Alkaline potassium permanganate is used as an oxidising agent in organic reactions.

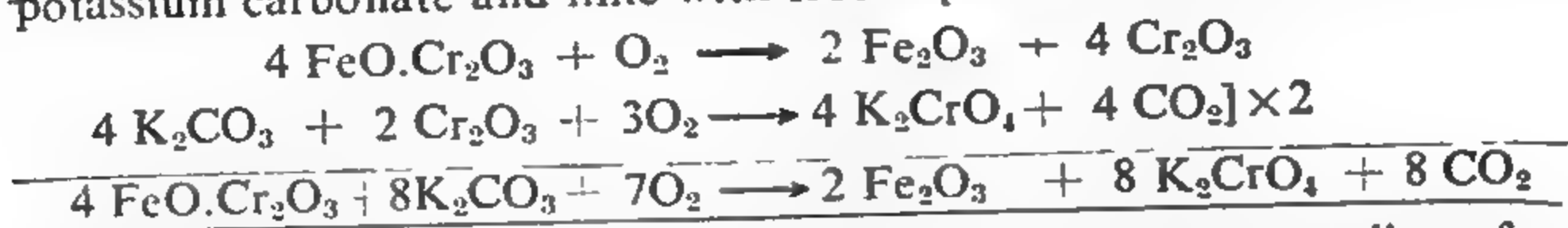
3. Potassium permanganate is also frequently used as a disinfectant.

Potassium Chromate, K_2CrO_4 . It is obtained by adding calculated amount of potassium carbonate to a solution of potassium dichromate.



The solution is evaporated to get lemon yellow rhombic crystals.

On a large scale, it is obtained from *chromite* ore, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. The ore is finely powdered and heated strongly in a reverberatory furnace with potassium carbonate and lime with free exposure to air :



The function of lime is to keep the mass porous so as to allow free access of air. After the reaction, the roasted material is extracted with hot water in an autoclave to dissolve potassium chromate and thus to separate it from the insoluble ferric oxide. On evaporating and cooling crystals of potassium chromate can be separated.

It is isomorphous with potassium sulphate, K_2SO_4 . It is very soluble in water, the solution is alkaline due to hydrolysis.



In acid solution, potassium chromate changes into dichromate and the colour of the solution changes from yellow to orange.



When heated to 670° , the yellow variety changes into a *red modification* which melts at 970° .

It is used in laboratory as an indicator in the volumetric estimation of chlorides by titrating against silver nitrate and as a reagent in qualitative analysis.

Potassium Dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$.

Preparation. It is prepared by adding a calculated amount of sulphuric acid to a saturated solution of potassium chromate.



It is manufactured by mixing hot saturated solutions of sodium dichromate (obtained from chromite ore in the same way as potassium chromate by replacing potassium carbonate with sodium carbonate) and potassium chloride



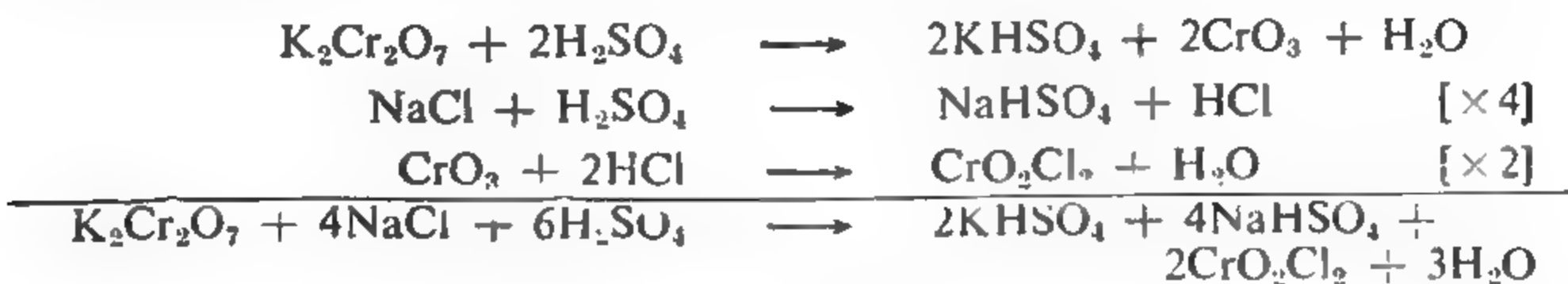
Sodium chloride precipitates out from the hot solution and is removed by filtration. On cooling the mother liquor, crystals of potassium dichromate separate out.

Physical Properties. Potassium dichromate forms orange-red crystals melting at 395° . It is moderately soluble in cold water but freely soluble in hot water.

Chemical Properties. 1. On strong heating it decomposes to give chromic oxide and oxygen.



2. Potassium dichromate, when heated with concentrated sulphuric acid and a soluble chloride, such as sodium chloride, gives red vapours of *chromyl chloride*.

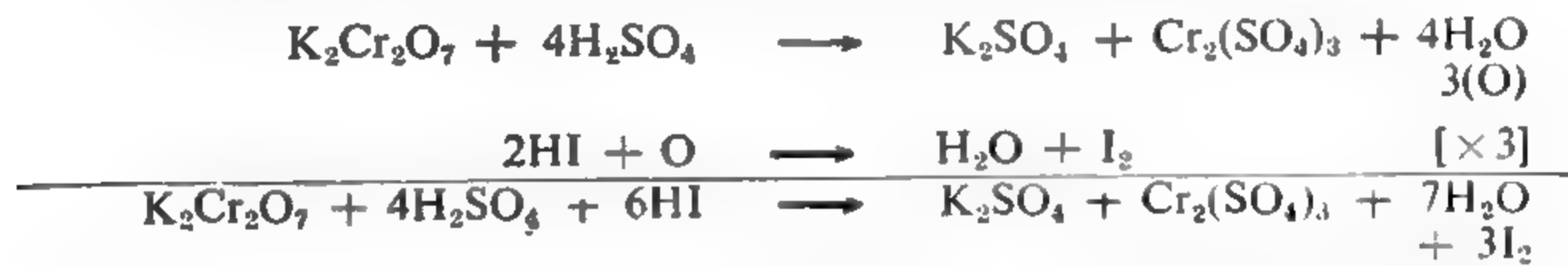


3. Potassium dichromate is a powerful oxidising agent. In the presence of dilute sulphuric acid, it can give oxygen readily which can be taken up by a reducing agent.

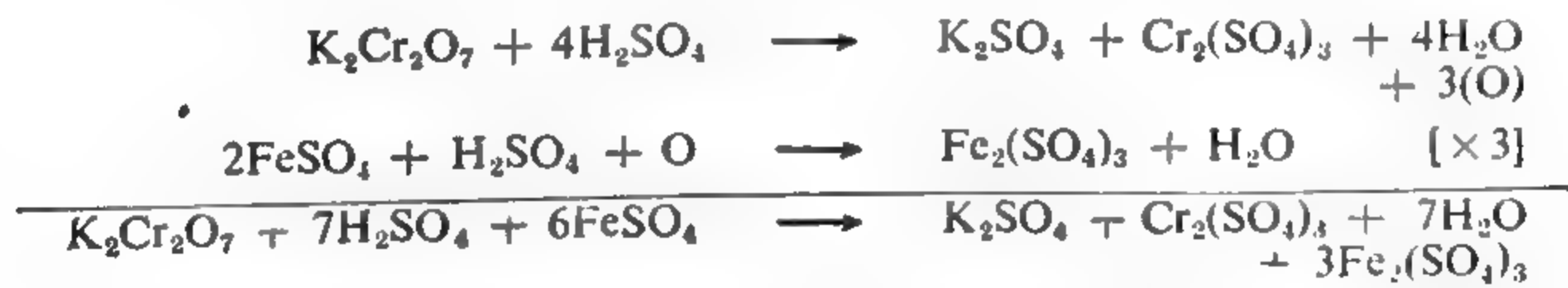


Typical oxidation reactions are given below :

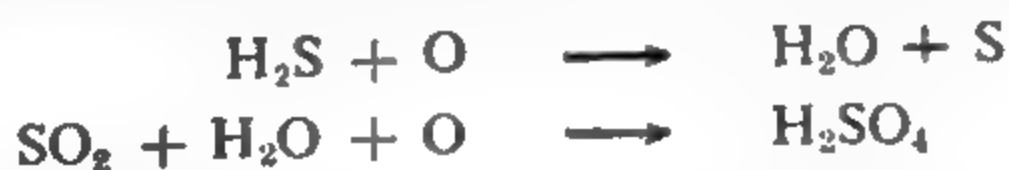
(i) *Liberation of iodine from potassium iodide solution.*



(ii) *Oxidation of Fe^{++} into Fe^{+++} , e.g.,*



(iii) *Oxidation of H_2S to S and SO_2 to sulphuric acid.*



(v) Potassium dichromate also oxidises alcohols first to aldehydes and then to acids.



4. On the addition of an alkali, the orange colour of dichromate solution changes to yellow due to the formation of chromate.



On acidifying, the yellow colour again changes to orange-red colour owing to the reformation of dichromate.



Uses. Potassium dichromate is used (i) as a volumetric reagent in laboratory for the estimation of ferrous ions, iodine, etc.

(ii) for the preparation of several chromium compounds such as chrome alum, chrome red (PbCrO_4 , PbO), zinc yellow (ZnCrO_4), chrome yellow (PbCrO_4), etc.

(iii) in dyeing, chrome tanning and calico printing.

(iv) in photography.

Bleaching Powder, $[\text{Ca}(\text{OCl})_2 \cdot 4\text{H}_2\text{O} + \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}]$ Bleaching powder is a mixture of calcium hypochlorite, $\text{Ca}(\text{OCl})_2$ and the basic chloride, $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$. It is prepared on a large scale by the action of chlorine on slaked lime.



In order to get good yield it is necessary to maintain close contact of chlorine with the slaked lime. The Hasenclever plant used for the purpose is shown in Fig. 15.2.

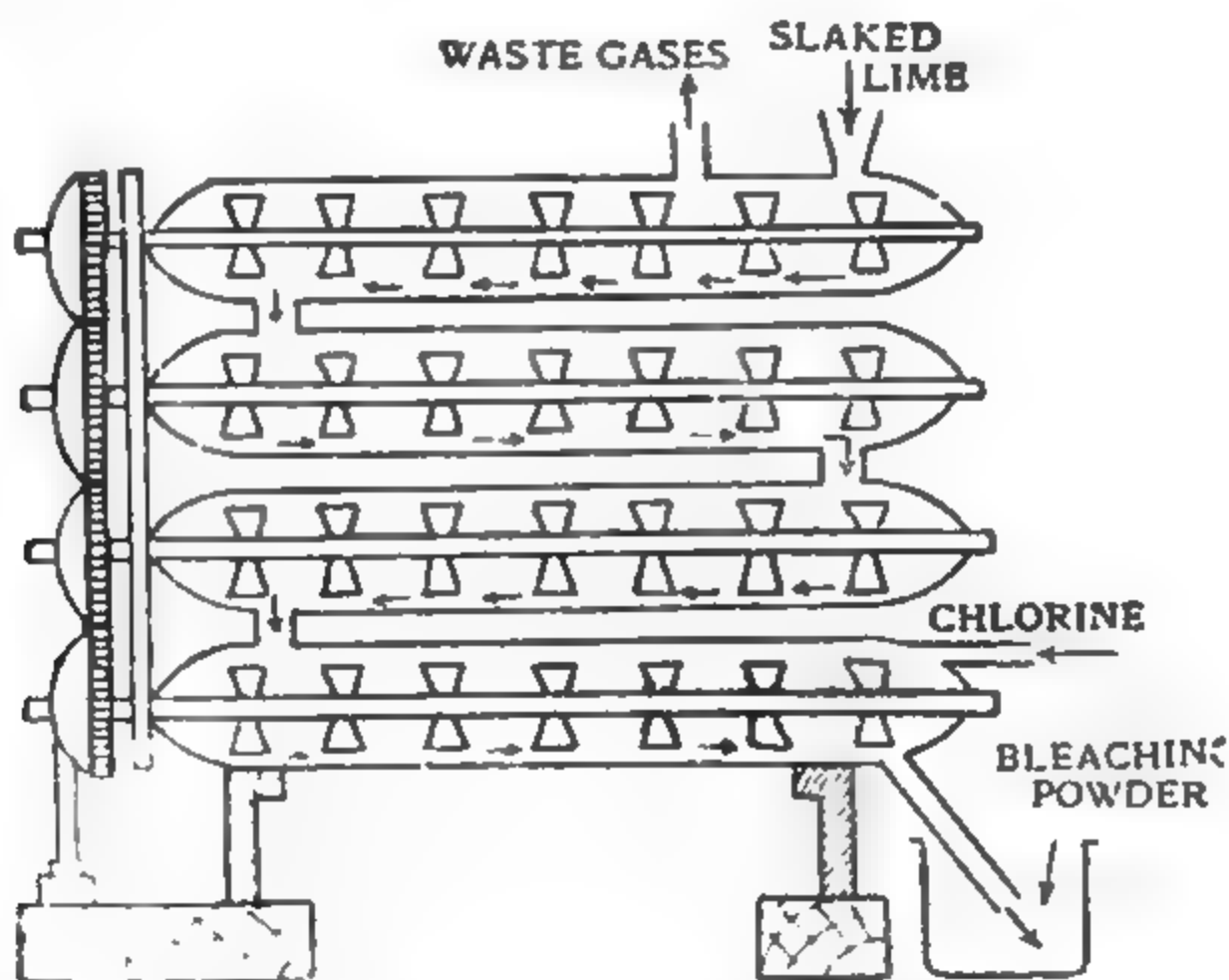


Fig. 15.2. Hasenclever plant for the preparation of bleaching powder.

It consists of a number of lead or iron pipes placed horizontally one above the other. Each pipe is provided with a rotating shaft fitted with blades. Chlorine is admitted into the apparatus through the lowermost pipe while lime is fed into the uppermost pipe through a hopper as shown. As the lime is made to traverse from one of the cylinders to the other by the action of the blades and then led into the next lower pipe, chlorine rises upwards and, thus, a close contact between the two is brought about. The rotation of the blades

keeps the lime in a constant tumbling motion so as to expose fresh surfaces to the action of chlorine. The reaction as represented in the equation above is not carried to completion because chlorine is not absorbed to that extent. The amount of chlorine actually absorbed depends upon the efficiency of the plant. The commercial value of bleaching powder depends upon the amount of *available* chlorine that it contains.

Recent method. These days, bleaching powder is generally prepared in **Bachmann's plant** (Fig. 15.3). It consists of a tall vertical tower made

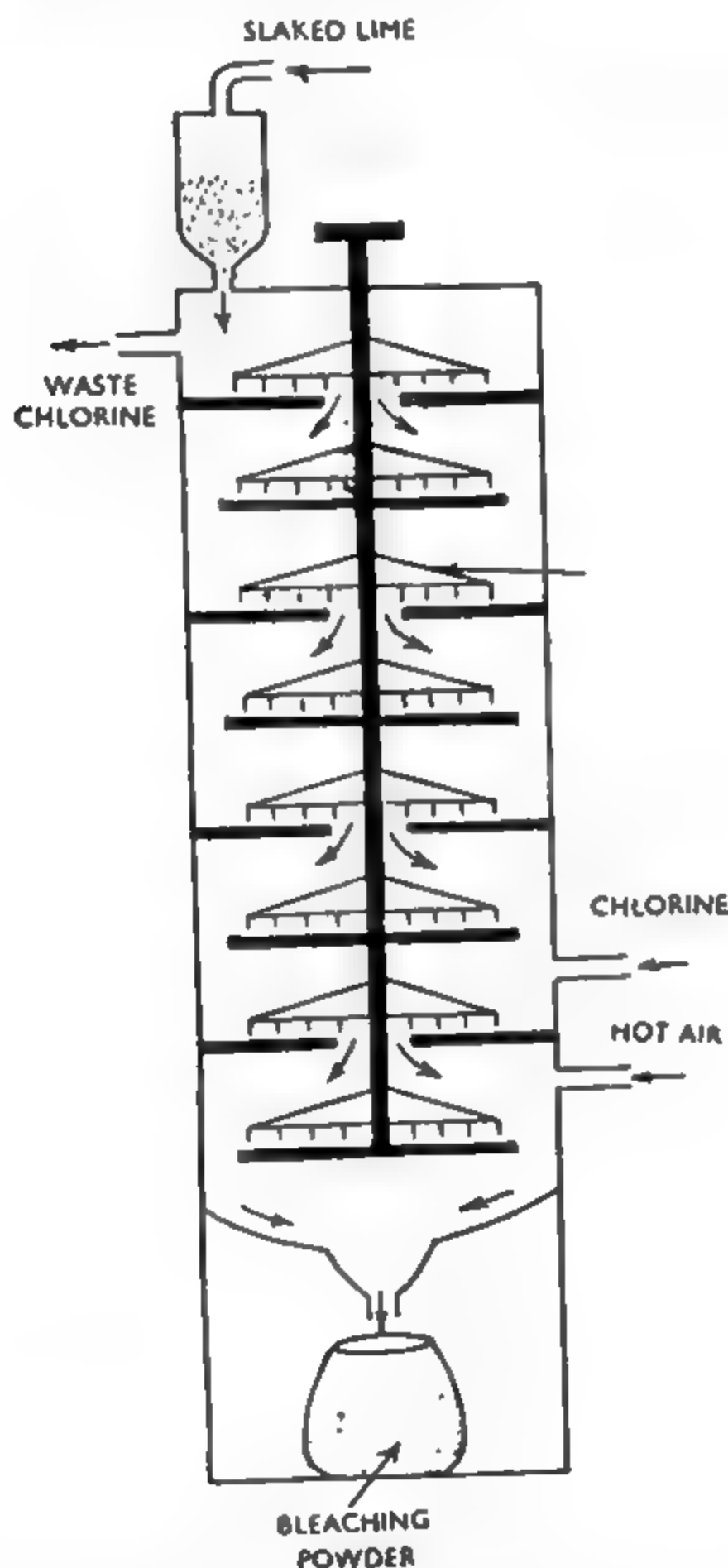


Fig 15.3. Bachmann's Plant for the manufacture of bleaching powder.

of cast iron provided with inlets for chlorine and hot air near the base and an outlet for waste chlorine at the top. The tower also carries a hopper at the top for admitting slaked lime. Inside the tower there are a number of horizontal shelves provided with rotating rakes.

The dry slaked lime is fed into the tower at the top through the hopper and a current of chlorine is admitted into the tower near the base. The slaked lime moves downwards from one shelf to an other with the help of the rotating rakes, meets an upward current of chlorine and gets converted into bleaching powder which collects in the container placed at the bottom as shown.

The current of hot air admitted near the base helps to drive away any unreacted chlorine through the outlet provided near the top.

Constitution of bleaching powder. There has been considerable speculation and research regarding the constitution of bleaching powder. On analogy with the reaction of chlorine with sodium hydroxide,



bleaching powder was regarded as a mixture of calcium chloride and calcium hypochlorite.



The presence of free calcium chloride was questioned by several workers on the ground that calcium chloride is deliquescent and soluble in alcohol whereas bleaching powder is neither deliquescent nor soluble in alcohol.

Odling, therefore, suggested that bleaching powder is a single chemical compound with the formula CaCl(OCl) , viz., *calcium chlorohypochlorite*.

This formula was accepted till quite recently. In 1935, Bunn, Clark and Clifford, by microscopic and X-ray examinations as well as by phase rule studies, established that bleaching powder is a mixture of calcium hypochlorite, $\text{Ca(OCl)}_2 \cdot 4\text{H}_2\text{O}$ and a *non-deliquescent* basic chloride of calcium, $\text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot \text{H}_2\text{O}$, in more or less equimolecular proportion. The basic chloride is insoluble in alcohol.

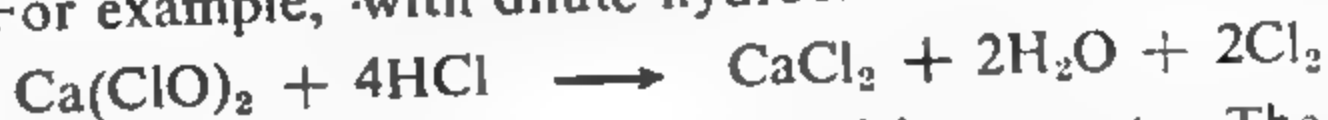
The first products of the chlorination of slaked lime are *basic hypochlorite*, $\text{Ca(OCl)}_2 \cdot 2\text{Ca(OH)}_2$ and *basic chloride* $\text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot \text{H}_2\text{O}$. On further chlorination, the basic hypochlorite is converted into the hypochlorite, i.e., $\text{Ca(OCl)}_2 \cdot 4\text{H}_2\text{O}$. Thus, ultimately, bleaching powder consists of a mixture of $\text{Ca(OCl)}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot \text{H}_2\text{O}$.

Properties. (1) Bleaching powder is a white solid with a slight yellowish tinge. It has the characteristic odour of chlorine. This is because of its slow decomposition by atmospheric carbon dioxide.

(2) It is slightly soluble in water and the solution gives the reactions of Ca^{2+} , OCl^- , OH^- and Cl^- ions as is expected from its formula discussed above.

(3) Bleaching powder liberates chlorine on treatment with dilute acids. The whole of the chlorine in bleaching powder is not rendered available. It is mainly the chlorine of the hypochlorite ion OCl^- , which

is given out on treatment with dilute acids and is known as **available chlorine**. For example, with dilute hydrochloric acid, the reaction is



Bleaching powder acts as a strong oxidising agent. The oxidising action is also due to the hypochlorite ion, which is reduced to the chloride ion. Thus, potassium iodide is oxidised to iodine.



This reaction is used for *estimating available chlorine* in bleaching powder. The method consists in treating the suspension of bleaching powder with excess of potassium iodide solution acidified with acetic acid. The liberated iodine is estimated by titrating against a standard solution of sodium thiosulphate.

The hypochlorite ion, being unstable, also breaks into oxygen as such.



This is also responsible for the bleaching action of bleaching powder.

Uses. (1) The main application of bleaching powder is in bleaching. This is used for bleaching paper pulp as well as cotton and linen goods. The bleaching property is evidently due to the available chlorine.

(2) It is also used as a disinfectant. It is scattered over the floors of hospitals or other buildings to be disinfected. It slowly liberates chlorine by the action of atmospheric carbon dioxide. It is also used for chlorination of drinking water.

(3) It renders wool unshrinkable. The wool is first well soaked in a very dilute solution of hydrochloric acid and then immersed in the suspension of bleaching powder. After this treatment, it is put in an *antichlor bath*, containing sodium thiosulphate to remove the excess of chlorine.

(4) It is also used in the manufacture of chloroform.

14. Process of Bleaching. The following steps are gone through :

(1) The cotton fabric is boiled with a dilute solution of caustic soda to remove grease or wax.

(2) The fabric is then dipped in a solution of bleaching powder where some bleaching takes place due to atmospheric carbon dioxide.

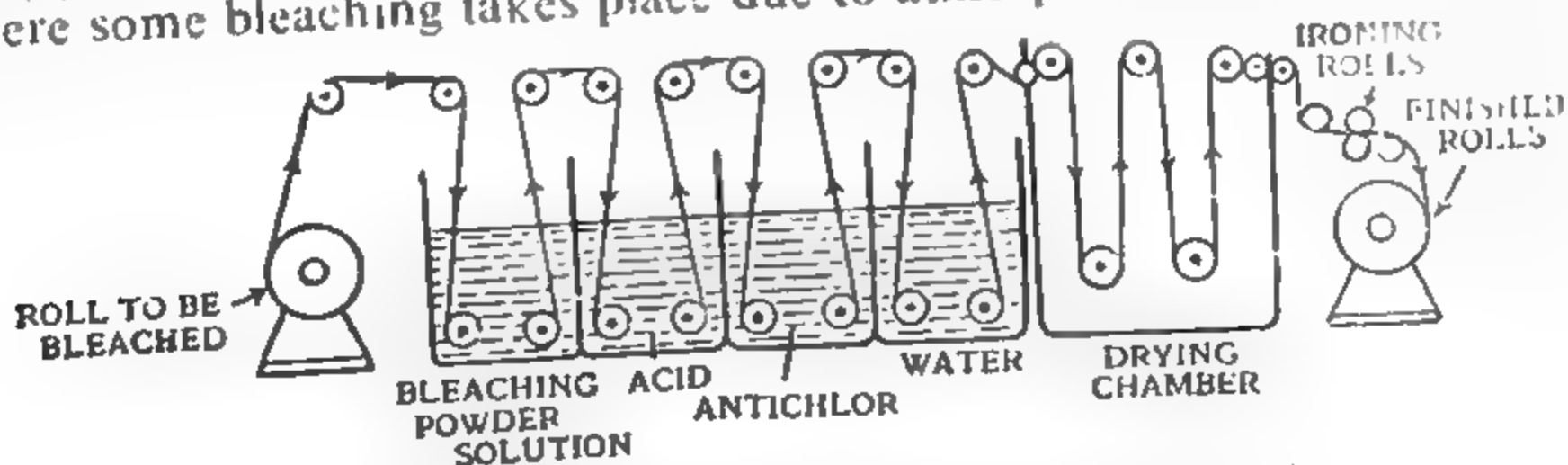
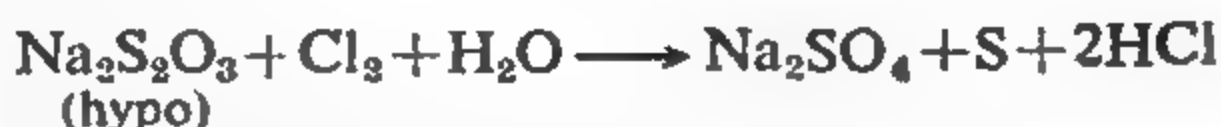


Fig. 15.4. Bleaching of cotton cloth in big factories with bleaching powder or bleaching solution.

(3) The fabric is then passed through a dilute acid solution. Chlorine is evolved and completes bleaching.

(4) The article is then passed through a solution of hypo or sodium bisulphite to remove the last traces of chlorine lest it should injure the fibre.



(5) Lastly, the fabric is washed with water. It is dried and ironed.

In factories, the process of bleaching is automatic as is shown in (Fig. 15.4).

Potassium Chlorate, KClO_3 .

Preparation. (1) It is prepared by passing chlorine through a hot solution of potassium hydroxide as mentioned above.

This method, however, is wasteful since nearly $5/6$ th of KOH is converted into potassium chloride. Therefore, for industrial production, calcium hydroxide, which is cheaper, is used instead of potassium hydroxide when the following reaction takes place :



The solution containing calcium chloride and calcium chlorate is concentrated to a small extent by evaporation and then potassium chloride is added in a slight excess. Calcium chlorate is, thus, converted into potassium chlorate.



Potassium chlorate, being much less soluble than calcium chloride or calcium chlorate, separates out readily on raising the concentration of the solution only slightly by evaporation. It can be purified by recrystallisation.

(2) Potassium chlorate is prepared now-a-days electrolytically, by electrolysing potassium chloride solution of about 25% concentration in cells made of iron. (Fig. 15.5). The temperature during electrolysis is maintained between $70-75^\circ$, by circulating hot water through a coil of iron pipe as shown in the figure. The exposed parts of the iron tank and the cooling pipe act as the cathode while a set of graphite rods act as the anode. In this way, the products of electrolysis, namely, potassium hydroxide and chlorine are quite close to one another to bring about their interaction.



A small amount of sodium dichromate is added to the solution to prevent the reduction of chlorate by the nascent hydrogen produced at the cathode.

The electrolysis is continued so as to get a saturated solution of potassium chlorate. On cooling, crystals of potassium chlorate separate out, leaving the more soluble potassium chloride in the mother liquor.

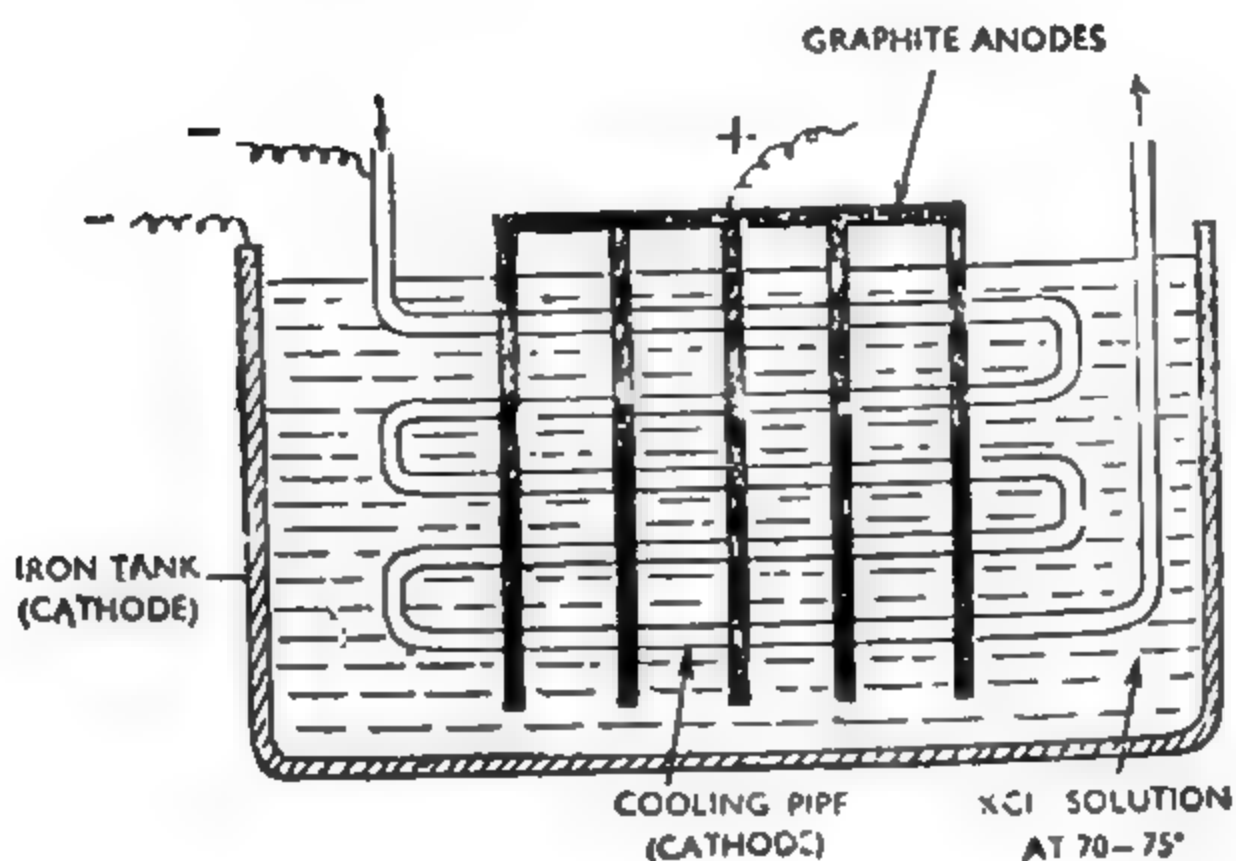


Fig. 15.5. Manufacture of potassium chlorate.

Properties. (1) It is a non-hygroscopic solid, highly soluble in water.

(2) It decomposes on heating. The decomposition takes place in two steps :

(i) In the first place, it undergoes *oxidation-reduction* disproportionation.

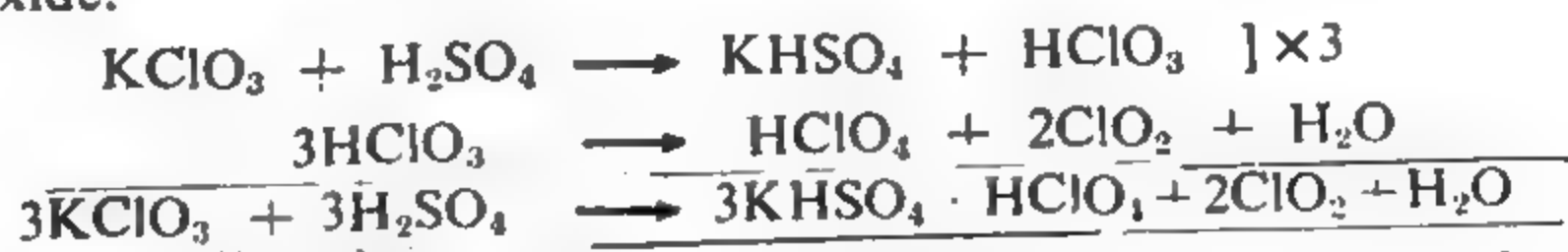


(ii) The perchlorate then decomposes at a higher temperature to evolve oxygen.



(3) Potassium chlorate as well as other chlorates are strong oxidising agents. If a mixture of potassium chlorate with an organic substance or charcoal or sulphur is heated or struck with a hammer, an explosion occurs. Explosion also occurs on adding a drop or two of a solution of phosphorus in carbon disulphide on potassium chlorate.

(4) On treatment with hot concentrated sulphuric acid, it evolves chlorine dioxide.



(5) On treatment with conc. hydrochloric acid, a mixture of chlorine and chlorine dioxide (**euchlorine**) is obtained.



(6) When treated with dilute sulphuric acid, it gives chloric acid.



Uses. Potassium chlorate is used in large amounts in the manufacture of safety matches. It is also used in the manufacture of explosives. In the laboratory, it is used for the preparation of oxygen. In dilute solutions, it is used as a mouth wash and also for gargling in case of sore throat.

Sodium Thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

1. It is prepared in the form of monoclinic crystals by boiling a solution of sodium sulphite with sulphur.



It is commonly known as 'hypo'.

2. In pure state, it is prepared by the cointeraction of sodium hydrogen sulphide and sodium hydrogen sulphite.



3. It is also prepared by treating a mixture of sodium sulphide and sodium sulphite with iodine.



Manufacture. There are two methods of its manufacture. The earlier method based on the reaction of sulphur dioxide with sodium carbonate (alkali waste) has now been largely replaced by the new method which is based on the reaction of sulphur dioxide with sodium sulphide (sulphide waste).

1. **From sodium carbonate.** A solution of sodium carbonate is saturated with sulphur dioxide as a result of which a solution of sodium sulphite is obtained :



Two absorption towers, made of lead and packed with hard wood-sticks are used for the purpose. These are operated on counter current principle. The fresh solution of sodium carbonate is allowed to trickle down the first tower where it meets an ascending stream of the spent gas from the top of the second tower. In this way, the residual gas is almost completely absorbed in the fresh solution. This solution is then pumped on to the top of the second tower from where it flows down and meets the fresh gas from the burners. In this way, sodium carbonate is completely converted into sodium sulphite.

This solution is then heated with sulphur in cast iron vessels lined with lead, with constant and vigorous stirring for a few hours when sodium sulphite changes into sodium thiosulphate.



The solution is allowed to cool to get crystals which are separated from the mother liquor in centrifugal machines.

2. From sodium sulphide. This method is more economical since sodium thiosulphate is obtained as a by-product in the manufacture of sodium sulphide from sodium sulphate.

After crystallisation of sodium sulphide, the waste mother liquor retains about 8—10 per cent of sodium sulphide besides 5—6 per cent of sodium carbonate. It is treated with sulphur dioxide in lead-lined towers working on the counter-current principle as in the method discussed above. The following reactions take place :



The liquid containing sodium thiosulphate is allowed to crystallise in lead-lined crystallising tanks as in the previous method.

Properties. 1. Sodium thiosulphate is a white crystalline solid (*m.p.* 48°). It is soluble in water. It loses its water of crystallisation at 215° and decomposes when heated above 220° , giving sodium sulphate and sodium pentasulphide.



2. On treatment with a dilute mineral acid, thiosulphuric acid is formed, which, however, decomposes instantaneously into sulphur dioxide and free sulphur.



The separation of sulphur along with evolution of sulphur dioxide serves as a test for distinguishing between a thiosulphate and a sulphite. In the latter case, there is no formation of sulphur.

3. On the addition of silver nitrate, a white precipitate of silver thiosulphate is obtained which, however, readily changes to yellow-brown and finally black due to its reduction into silver sulphide.



4. Sodium thiosulphate decolorises iodine solution forming sodium tetrathionate.



This reaction is made use of in volumetric estimation of iodine.

5. Sodium thiosulphate gives a purple coloration on the addition of ferric chloride.



6. It reacts with chlorine giving hydrochloric acid.



Hence, it is used as an antichlor.

3995
2995

Tests. Reactions numbered 2, 3, 4 and 5 given above are used as tests for thiosulphates.

Uses. 1. Sodium thiosulphate is largely used in photography as a 'fixing agent'. It reacts with the unreduced silver bromide.



2. It is used as an antichlor due to its reaction with chlorine.

3. In laboratory, it is used in volumetric estimation of iodine.

Chromic Compounds-used as Pigments.

Several compounds of chromium are used as pigments in pottery glazes, building paints, printing colours, etc. They give fast and stable colours. The important compounds are discussed below :

Lead chromate, PbCrO_4 , Chrome yellow. It has a brilliant yellow colour and is prepared by adding a solution of sodium dichromate to a solution of lead nitrate or acetate. It is the least soluble salt of lead.

Another pigment known as **chrome green** is obtained by mixing intimately chrome yellow with prussian blue.

Basic lead chromate, $\text{PbCrO}_4 \cdot \text{PbO}$, Chrome red. It is a bright red pigment made by digesting lead chromate with a dilute alkali. Mixed with lead chromate, it is used as *chrome yellow*.

QUESTIONS

1. How is potassium permanganate prepared ? Discuss its oxidising properties and uses.
2. Describe the preparation of potassium permanganate from pyrolusite. Discuss the oxidising action of the compound in (i) solid state (ii) acidic medium (iii) alkaline medium (iv) neutral solution.
3. How is potassium chromate prepared ? Describe its properties and uses.
4. Describe the preparation, properties and uses of potassium dichromate.
5. Describe the preparation of bleaching powder. How has its constitution been established ?
6. Discuss the constitution of bleaching powder. What is meant by available chlorine ? Give the important uses of bleaching powder.
7. Describe the preparation, properties and uses of potassium chlorate.
8. How is potassium chlorate prepared on a commercial scale ? Describe the action of hydrochloric acid and sulphuric acid on the compound.
9. What is hypo ? How is it prepared ? To what uses is it put ?
10. Describe the preparation, properties and uses of sodium thiosulphate.
11. Write short notes on :
(1) Chrome yellow (2) Chrome red (3) Chrome green.

PART II
ORGANIC

CHAPTER XVI

INTRODUCTION

Division of Chemistry. Towards the close of the seventeenth-century a group of scientists headed by Lemery suggested that chemical compounds should be classified according to their origin. Lavoisier and a number of other chemists developed this idea about a hundred years later and divided the various substances known at that time into two categories :

1. *Those obtained from living organisms (plants and animals) were called organic.* The examples are : fats, oils, sugars, urea. It was found that all organic compounds contain carbon as an essential element.

2. *Those obtained from inanimate matter (minerals and rocks) were called inorganic.* The examples are : common salt, nitre, limestone, iron, sulphur, gypsum.

Both organic and inorganic compounds continued to be studied together for another century. But towards the close of the nineteenth century the number of compounds that came to be known increased so much that it was felt more convenient to study organic compounds separately from inorganic compounds. Chemistry was, therefore, divided into two branches :

(1) **Organic chemistry** which deals with the study of organic compounds, *i.e.*, carbon compounds, and

(2) **Inorganic chemistry** which confines itself to the study of inorganic substances, *i.e.*, metallic and non-metallic elements and their compounds.

A third major branch of chemistry, known as **physical chemistry**, also developed soon after. It concerns itself with the study of physical properties and constitution of matter and the laws and theories governing chemical reactions.

Vital Force Theory In the early nineteenth century it was realised by a number of investigators that while inorganic compounds could be

prepared in the laboratory, *organic compounds could not be so prepared*. Berzelius, in 1815, attributed this difference to the existence of some mysterious force (which he called *vital force*) in living organisms which alone could produce organic compounds.

This vital force theory soon proved to be a myth. In 1828, Wohler, a student of Berzelius, while preparing ammonium cyanate, accidentally prepared urea, a substance till then known to occur in urine only. Thus, urea, a typical organic compound, could be prepared from inorganic materials as shown below :



This led to the preparation of some other organic compounds in the laboratory. Kolbe in 1843 synthesised acetic acid from its elements, namely, carbon, hydrogen and oxygen. Berthelot in 1856 prepared methane starting with purely inorganic materials. This sealed the fate of vital force theory. The belief in the unknown mysterious force exclusively responsible for the formation of organic compounds was completely shattered. Organic compounds could be prepared in the laboratory just like inorganic compounds. The word 'organic' (pertaining to life) lost its original significance. **Organic compound** was given a more logical definition *as a compound containing carbon* and **organic chemistry** was defined as *the chemistry of carbon compounds*. However, a few compounds of carbon such as carbon dioxide and carbon disulphide still continue to be studied in inorganic chemistry.

Reasons for separate treatment of organic chemistry. It may be stated at the very outset that the same fundamental principles are involved in both organic and inorganic chemistry. The main reasons for treating the two branches, organic and inorganic, separately are :

(i) Organic compounds are made up of only a few elements, namely carbon, hydrogen, oxygen, nitrogen, sulphur and the halogens. Inorganic compounds, on the other hand, consist of any of the 103 elements known at the present day.

(ii) Carbon, the essential element in organic compounds, has the unique property of combining with other carbon atoms to form either straight chain or side chain or ring compounds. Thus there is a greater variety of compounds in organic than in inorganic chemistry.

(iii) The number of organic compounds known (over 750 000) far exceeds the number of inorganic compounds (less than 40,000). Other points of difference between the organic and inorganic compounds are given in Table I.

TABLE 1.

Points of Difference between Organic and Inorganic Compounds

Property	Organic Compounds	Inorganic Compounds
1. Type of linkage involved.	Largely covalent	Largely electrovalent
2. Solubility in water	Generally low	Generally high
3. Conductivity in aqueous solution	Low	High
4. Solubility in organic solvents.	High	Low
5. Melting points	Low	High
6. Boiling points	Low	High
7. Velocity of Reactions	Very low	Very high
8. Combustibility	Generally combustible	Generally incombustible (with several exceptions)
9. Isomerism	Show isomerism (<i>i.e.</i> , one molecular formula may represent different compounds with altogether different properties).	Do not show isomerism (<i>i.e.</i> , one molecular formula represents one compound only)

The above differences indicate general tendencies. There are several exceptions, however. For instance, while most of the organic compounds are insoluble in water, ethyl alcohol, acetic acid, sugars and diazonium salts are freely soluble in water.

Sources of Organic Compounds. Organic compounds are derived mainly from natural sources such as plants and animal tissues. For instance, rubber, vegetable oils, perfumes, alkaloids, carbohydrates and even alcoholic beverages are derived directly or indirectly from plants. The animal perfumes (such as musk and mastic), milk, fats, urea, and oils are produced by animals. In modern times, two other important sources of organic compounds have attracted the attention of scientists and technologists. They are petroleum and coal. From petroleum such useful materials as gasoline, lubricating oil, paraffin wax, jet fuel and diesel oil have been isolated and put to innumerable applications. Coal has yielded coke and coal tar—a substance which has been found to be the stockhouse of a large number of useful products such as perfumes, dyes, disinfectants and a vast number of other products of great industrial importance.

Apart from natural sources, a large variety of organic compounds have been synthesised in laboratory or obtained by fermentation processes.

Importance of Organic Compounds. A number of organic compounds are of wide interest from fundamental as well as applied point of view. They have opened up a new horizon of our knowledge regarding the structure of molecules and mechanism of the various reactions taking place in living organisms. The important constituents of our food such as carbohydrates, fats and proteins are organic materials derived mainly from plant and animal tissue. Besides food, the body needs vitamins, hormones and enzymes for its growth and sustenance. All these materials are organic in nature.

The contributions made by organic chemistry in the field of industry, agriculture, health and medicine have been almost unparalleled. The synthesis of a large number of dye stuffs from readily available and inexpensive raw materials, manufacture of different kinds of plastics such as synthetic rubber, thermoplastic, polyethylene polystyrene and resins; discovery of synthetic fibres such as rayon, nylon, terylene, and arlon; preparation of essential oils such as camphor and terpenes; introduction of antiseptics such as formaldehyde, salicylic acid, iodoform, mercurochrome, chloramine T, gentian violet, thymol and dettol, development of insecticides such as D.D.T. and gammexane; making new anaesthetics such as chloroform, cyclopropane and terilene; manufacture of antipyretics (which lower body temperature in fever) such as phenacetin and aspirin, putting up of narcotics and hypnotics (which relieve pain and induce sleep) like morpine, sulphonal and butyl barbitol; study of natural drugs like quinine, nicotine, and synthetic chemotherapeutic drugs and antibiotics (which are poisonous to disease-carrying bacteria but do not harm the patient) such as sulphanilamide, sulphapyridine, sulphaguandine, penicillin, streptomycin, terramycin, choloromycetin; production of a large variety of cosmetics and detergents such as soaps, creams, shampoos and other toilet materials, etc., have revolutionised the modern way of life.

QUESTIONS

1. What are the reasons for treating organic chemistry separate from inorganic chemistry?
2. Give important differences between organic and inorganic compounds.
3. What is the 'Vital Force' theory? What led to its downfall?
4. What are the important sources of organic compounds?
5. Describe the importance of organic chemistry in everyday life and industry.
6. "Organic chemistry has revolutionised the modern way of life." Justify the statement with examples.
7. Enumerate the sources of organic compounds and in support give names of the two organic compounds derived therefrom.
(Punjab Inter 1960)
8. Write a concise note on applications of organic chemistry in everyday life.
(Punjab Inter 1960 S)
9. What are important differences between organic and inorganic compounds?
(Madras Inter. 1955)

CHAPTER XVII

THE INVESTIGATION OF ORGANIC COMPOUNDS

When an organic compound has been prepared in the laboratory or obtained from any one of the natural sources mentioned in the previous chapter, it is examined in the following stages :

(1) **Purification.** There is no use of analysing a compound unless it is pure because the presence of impurities will lead to wrong conclusions. Therefore, the first stage is to purify it. The common methods used for the purpose are described in the next chapter.

(2) **Qualitative Analysis.** The purified substance is then analysed *qualitatively* to find the elements contained in it. The elements commonly present (besides carbon which is always there) are hydrogen, oxygen, nitrogen, the halogens, sulphur, phosphorus and metals.

(3) **Quantitative Analysis.** After knowing qualitatively the various elements contained in the substance, the next step is to find out, by suitable methods of analysis, the percentage composition of the substance, that is, the amount of each element contained per 100 gm. of the substance. Oxygen is usually obtained by difference. Suppose a compound is found by analysis to have C=28.5 per cent; H=14.5 per cent; Cl=22.0 per cent. Then the percentage of oxygen = $100 - (28.5 + 14.5 + 22.0) = 35.0$.

(4) **Empirical Formula.** From the percentage composition of the compound it is possible to calculate its **empirical formula**, that is, the *simplest formula which gives the relative number of the atoms of the various elements contained in a molecule of the substance*. The empirical formula may not be the actual formula of the compound. It merely indicates the simplest *ratio* in which the atoms of the various elements are present in the compound.

A compound in which carbon, hydrogen and oxygen are present in the ratio of 1 : 2 : 1, will have the *empirical formula* CH_2O . The *empirical formula weight* will be $12 + 2 + 16 = 30$.

(5) **Molecular Formula.** The molecular formula of a compound gives the *actual number of the atoms of the various elements constituting a molecule of the compound*. The above compound having the empirical formula CH_2O may have the same molecular formula or some simple multiple of it. In other words, the molecular formula may be CH_2O or $\text{C}_2\text{H}_4\text{O}_2$ or $\text{C}_3\text{H}_6\text{O}_3$, etc. In order to decide between these various formulae the next step in the systematic investigation is the determination of

molecular weight of the compound by any of the suitable processes described in Chapter XXI. Suppose the molecular weight is 30, that is, the same as the empirical formula weight. Then the molecular formula of the compound will be the same as empirical formula, viz. CH_2O . If the molecular weight is 60, the molecular formula will be $(\text{CH}_2\text{O})_2$, that is, $\text{C}_2\text{H}_4\text{O}_2$. In other words,

$$\text{Molecular formula} = (\text{Empirical formula}) \times n$$

$$\text{where } n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

(6) **Constitutional or Structural Formula.** The molecular formula merely expresses the actual number of the atoms of different elements present in a molecule of the compound. It does not indicate the *constitution of the compound*, that is, *the manner in which the various atoms are arranged within the molecule*. In organic chemistry two or more arrangements of the atoms are possible thus giving rise to two or more *different* compounds altogether. For example, there are two compounds having the same molecular formula, $\text{C}_2\text{H}_6\text{O}$;



In such cases it is necessary to *examine the chemical reactions of the compound* in order to decide, in the above case, for instance, whether the compound contains a hydroxyl group ($-\text{OH}$) or an ether group ($-\text{O}-$).

(7) **Synthesis.** Having arrived at the constitutional or structural formula of the compound, the final step is to plan its synthesis from ordinary raw materials, often starting with carbon and hydrogen. If the planned synthesis is successful, the constitution of the compound is confirmed. Not only this. The synthesis of a large variety of useful but rarely occurring substances such as hormones, vitamins, dyes, drugs, etc., have resulted in their wider availability at very low cost. Therein lies the great utility and importance of organic chemistry.

The various stages outlined above have been discussed in details in the succeeding chapters.

CHAPTER XVIII

PURIFICATION OF ORGANIC COMPOUNDS

The importance of purifying an organic compound in systematic investigations has already been emphasised.

The common methods employed for the purification of solids and liquids are :

- (1) *Crystallisation.*
- (2) *Sublimation.*
- (3) *Extraction by means of a suitable solvent.*
- (4) *Distillation under ordinary pressure.*
- (5) *Distillation under reduced pressure.*
- (6) *Steam distillation.*
- (7) *Fractional distillation.*

PURIFICATION OF SOLIDS

1. Crystallisation. This is the most common method employed in the purification of a solid compound. The solvent used may be water or any other suitable organic liquid. This process involves the following steps :

(i) **Selection of the solvent.** The solvent selected should be such that either it does not dissolve the impurities at all or dissolves them to such a large extent that they remain in the mother liquor after separation of the solid in the form of crystals. In order to get good yield, it is also necessary that the solvent should dissolve more of the solid when hot than when cold. In other words, the solvent selected should be such that it dissolves the maximum quantity of the solute when hot and throws out the maximum quantity when cooled. The common solvents in use are given below. Their boiling points are given in brackets :

Benzene (82.2°) ; toluene (110.6°) ; petroleum ether ($50-60^{\circ}$) ; methyl alcohol (65°) ; ethyl alcohol (78.3°) ; acetone (56.2°) ; ethyl acetate (77.1°) ; acetic acid (118°) ; denser chloroform (61.2°) ; carbon tetrachloride (76.8°), etc.

(ii) **Preparing the solution.** The crude material is powdered and a suitable amount is taken in a conical flask. A small volume of the solvent

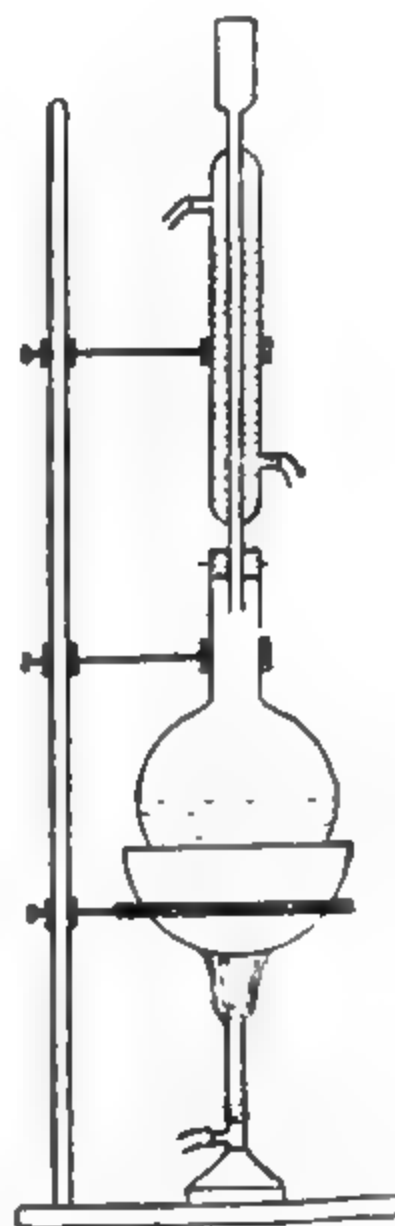


Fig. 1. Heating under reflux condition.

which is just insufficient to dissolve the whole of the material is then added. If the solvent is water, the mixture is gently heated over a naked flame to boiling. If it is one of the organic liquids, heating is done on a sand bath or a water bath. At the same time, the flask is fitted with a reflux (water) condenser, as shown in Fig. 1, to avoid the loss of the solvent. Sometimes it is more convenient to use a simple long glass tube (air condenser) in place of the water condenser.

(iii) **Filtering.** The hot and nearly saturated solution prepared in water or in any organic solvent in the above manner is then filtered. Care

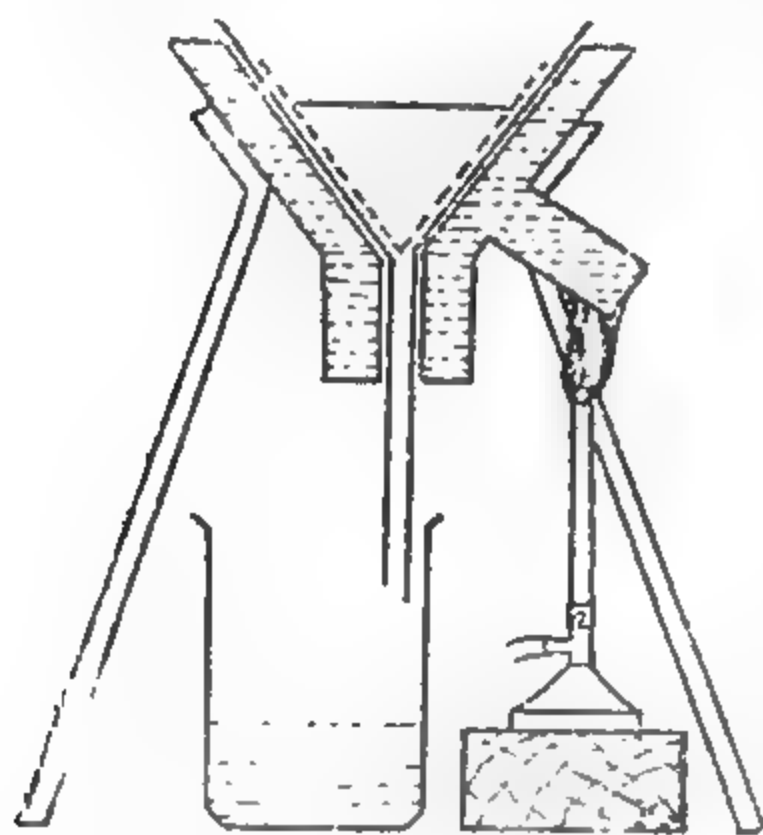


Fig. 2. Hot water funnel

must be taken to prevent undue cooling of the solution during filtration, otherwise crystals will separate out prematurely and choke the filter and the stem of the funnel. This is particularly so when large volumes have to be filtered. It is necessary, therefore, to use a **hot water funnel** (Fig. 2) which is an ordinary funnel surrounded by a metal jacket containing hot water.

(iv) **Crystallising.** The hot filtered solution is immediately transferred into a petri dish covered with a watch glass, and allowed to cool slowly if large crystals are required or rapidly if smaller crystals are desired. As cooling proceeds, the solution may be gently stirred by scratching the sides of the vessel from time to time. This often

facilitates crystallisation. The cooling should be continued for 15–20 minutes after the complete separation of the crystals.

It may be noted that the insoluble impurities had been removed earlier during filtration and the soluble impurities remain in the mother liquor and do not come out with the crystals.

(v) **Separation and drying of crystals.** The crystals and the mother liquor are transferred to a Buchner funnel fitted with a filter pump and connected to water tap as shown in Fig. 3. The mother liquor passes down into the filtration flask facilitated by the suction created by the filter pump. The crystals remaining on the filter paper are washed two or three times with a small quantity of the pure solvent so as to remove any adhering impurities. The suction is maintained so as to dry the crystals as far as possible. For further drying, the crystals may be pressed

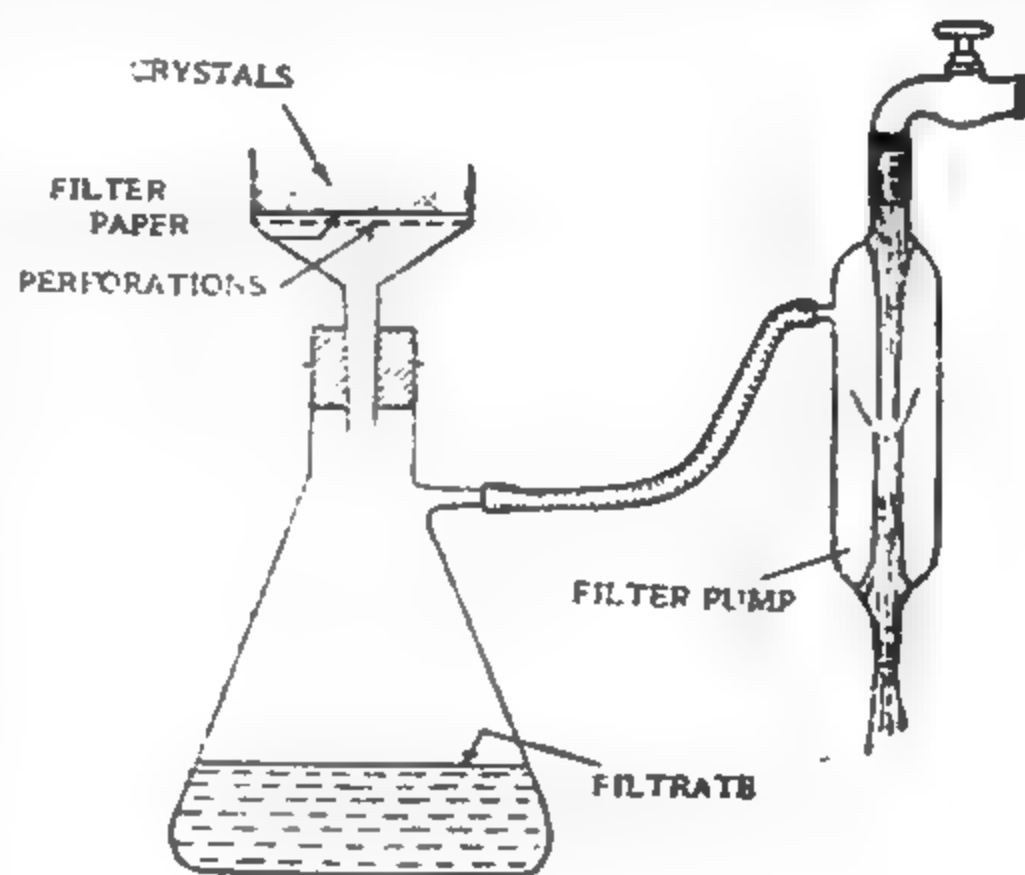


Fig. 3. Filtration under suction.

between two pads of filter paper or transferred to a porous plate and

dried in air or in an oven depending upon the nature of the substance. Quite often the crystals are dried over sulphuric acid or anhydrous calcium chloride in a vacuum desiccator (Fig. 4).

Sometimes the crystals obtained are a bit coloured due to the presence of traces of certain impurities. In such cases, the crystals are redissolved in a small amount of the solvent and a little of animal charcoal is added. The suspension is boiled for a few minutes and then filtered and crystallised as before.

2. Sublimation. Sublimation is a process in which a solid substance on heating passes directly into vapour state and the vapours when cooled condense directly to the solid state. This process is very helpful in purifying solids which sublime provided the impurities to be removed are non-volatile. By this method only a few substances can be purified.

The method consists in placing the impure material on a clock glass dish and covering this with an inverted funnel the stem of which is plugged with cotton and the sides of which are kept cooled (Fig. 5a). The clock glass or the dish is heated gently when the substance capable of subliming, is volatilised and the vapours are deposited on the inner cooled surface of the funnel leaving the non-volatile impurities in the dish.

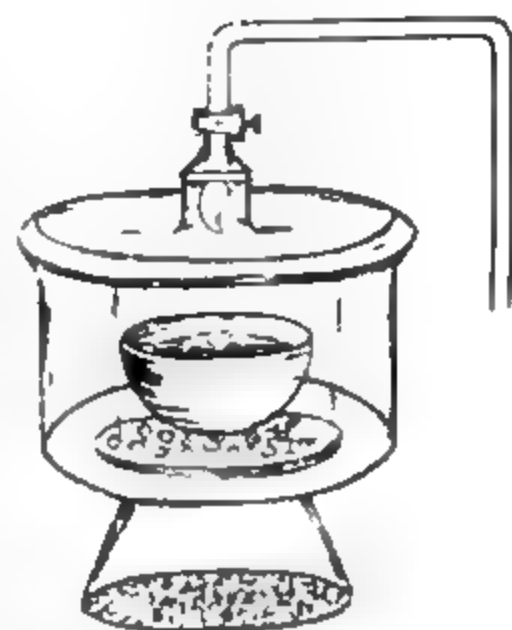


Fig. 4. Drying in a vacuum desiccator.

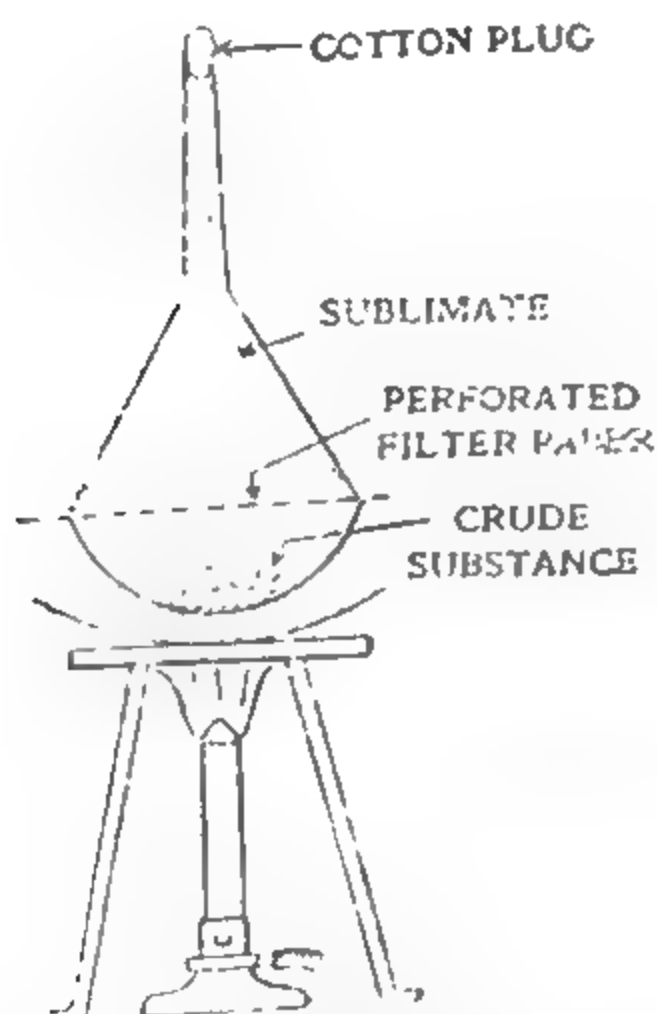


Fig. 5. (a) Sublimation.

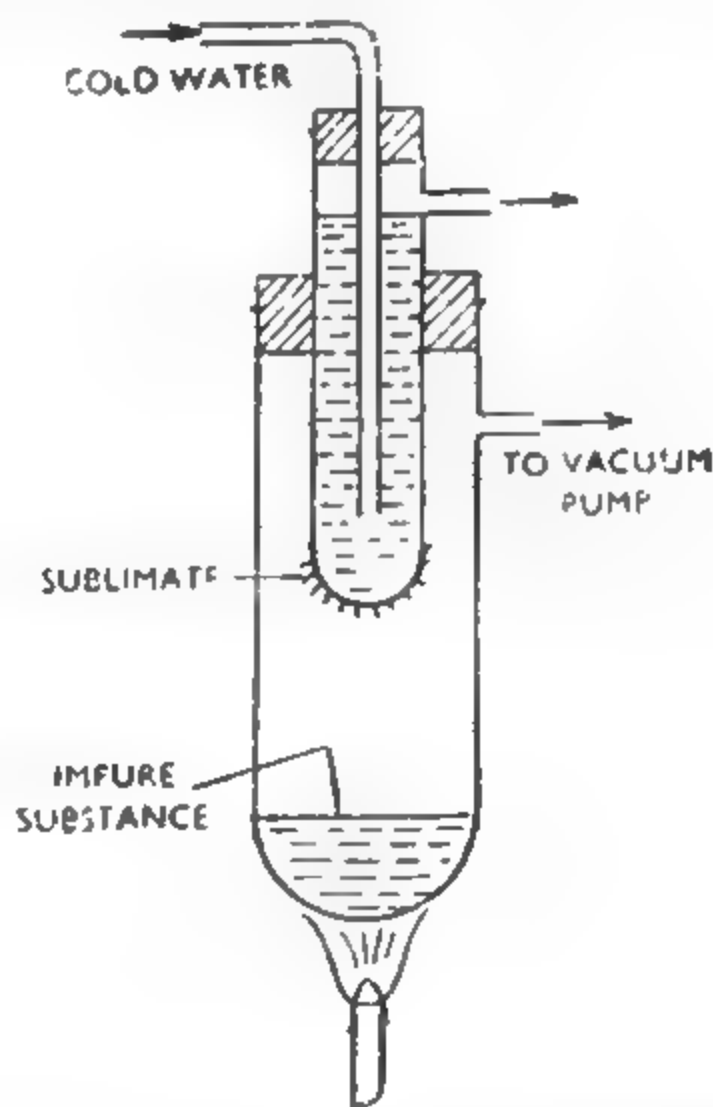


Fig. 5. (b) Sublimation under reduced pressure.

The dish is generally covered with a perforated filter paper which checks the sublimate from falling back into the dish.

Sublimation under reduced pressure. Those substances which are liable to decompose on heating are purified by sublimation under reduced pressure (cf. Fig. 5 b).

3. **Extraction by means of a Solvent.** This method is often used when the substance to be purified is present in aqueous solution or as suspension but is largely soluble in one or the other of the various organic solvents. Ether, chloroform and benzene which are sparingly soluble in water, are generally used. The method consists in mixing the aqueous solution with a small amount of the organic solvent (say ether) in a *separating funnel* (Fig. 6.) and shaking the contents vigorously for a few minutes. On allowing the mixture to settle, the two liquid layers separate from one another, the aqueous layer (being heavier) at the bottom and the ethereal layer at the top. By opening the tap the lower aqueous layer is taken out. The upper ethereal layer is then transferred to a stoppered bottle. The aqueous solution is shaken again once or twice with ether in a similar manner to extract more of the substance. The ethereal extracts are then combined and filtered. The solute, if solid, is separated by crystallisation and if liquid, by the process of fractional distillation.

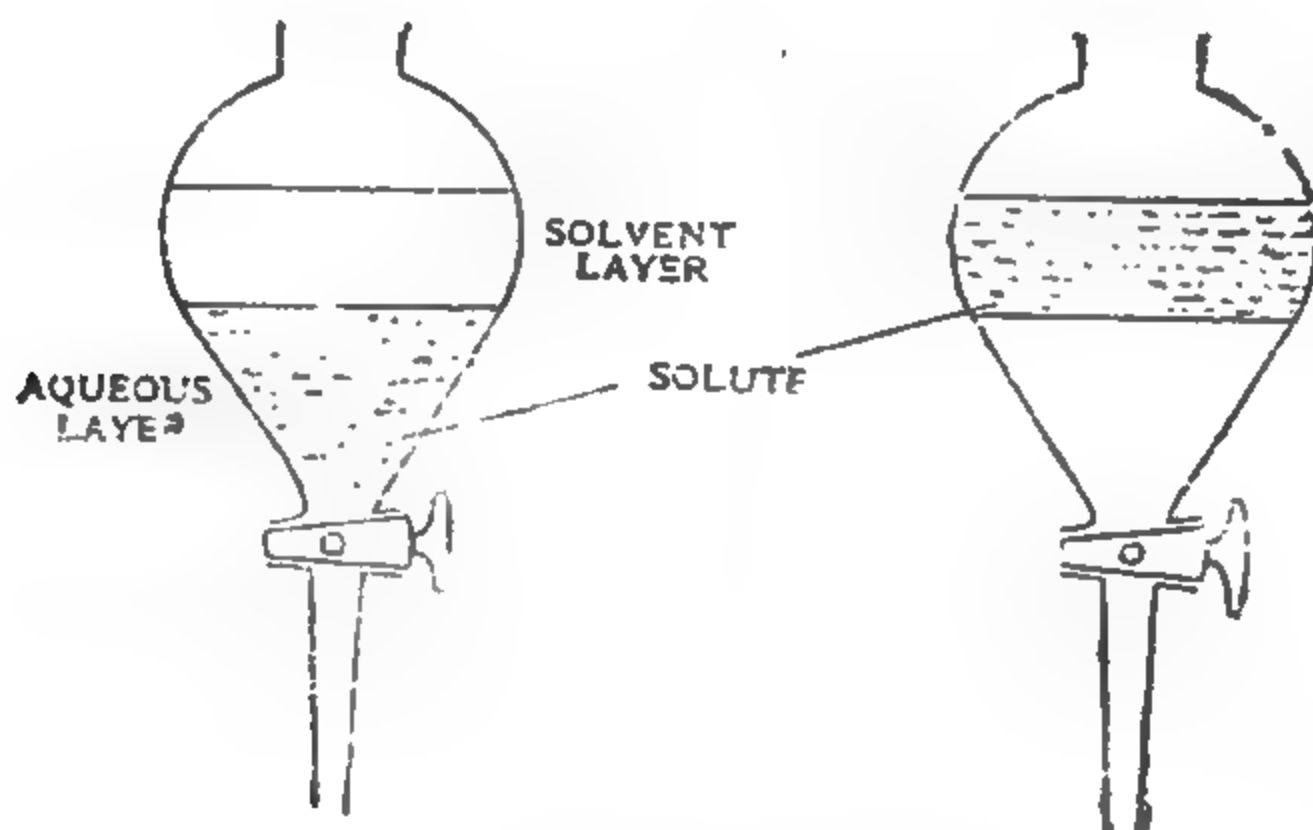


Fig. 6. A Separating funnel

Continuous Extraction. Soxhleting. Sometimes it is desired to obtain a pure product from some crude naturally occurring material. For instance, it may be required to isolate oil from seeds.

The first thing is to select a suitable solvent which will dissolve only the required constituent but not the rest. Ether or chloroform are generally used for this purpose. Only a small quantity of the solvent is taken and it can be used over and over again.

The apparatus used is known as Soxhlet's extraction apparatus and is shown in Fig. 7.

It consists of a glass cylinder *C* provided with a side tube *T* on one side, a siphon *S* at the other and a water condenser at the top as shown in the figure. The crude material from which the substance is to be extracted is placed in a porous thimble (shown by dotted lines) which is placed within the cylinder *C*. The height of the thimble is a little more than that of the siphon tube. The apparatus is then fitted into a flask containing the required solvent.

The flask is heated gently on a water bath or a sand bath so that the solvent begins to boil. The vapours pass up through the side tube *T* into the water condenser above and condense to liquid which falls down into the thimble and slowly fills the body of the cylinder *C* and dissolves the required organic substance from the crude material.

When the condensed liquid reaches the top of the cylinder *C*, it siphons back into the boiling flask. The solvent is heated and vaporised again as before while the extracted substance remains behind in the flask. The process repeats itself a number of times so that more and more of the organic substance gets extracted and transferred to the flask along with the solvent. Ultimately, the whole of the substance gets extracted from the crude material. Finally, it is isolated from the solvent by any suitable method such as distillation, etc.

Soxhlet's extraction apparatus is frequently used not only for the extraction of oils and fats from seeds and flowers but also for the extraction of alkaloids and other natural products from plants.

Chromatography. Recently a new analytical technique, known as 'chromatography' has been developed and extensively employed for separation and purification of organic compounds, especially those from natural sources (viz., plants and animals).

This technique, originally discovered by the Russian botanist Tswett in 1906, is based upon the fact that different constituents of a mixture on being poured down a column of a suitable adsorbent (e.g. alumina, silica gel, chalk) are *adsorbed to different extents*. A suitable organic solvent (ether, petroleum ether, benzene, etc.) is then passed down which separates the constituents into distinct bands. These constituents are selectively eluted by suitable solvents and collected separately. By suitable treatments, each of the fractions usually yields a different constituent.

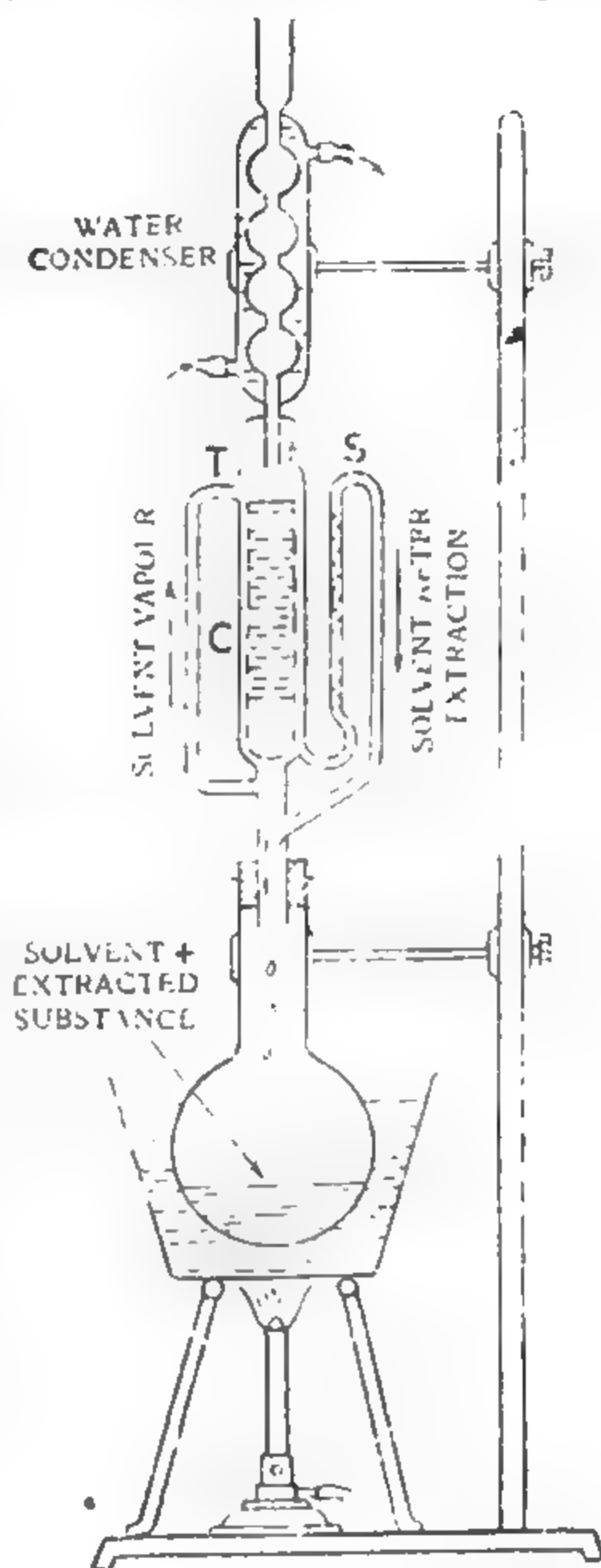


Fig. 7. Soxhlet's Extraction apparatus.

For instance, using chromatographic analysis., Tswett separated chlorophyll, the colouring matter of the plants, into two chlorophylls 'a' and 'b', xanthophyll and carotenes.

This technique has lately been used industrially also. Several types of chromatography are now used such as 'displacement chromatography,' partition chromatography, adsorption chromatography, liquid—gas partition chromatography, etc.

PURIFICATION OF LIQUIDS

Liquids are generally purified by the process of distillation. There are several ways of distillation each of which requires a special mention.

4. Distillation Under Ordinary Pressure. If the liquid to be purified has comparatively a low boiling point and does not decompose before its boiling point is reached, it may be purified by simple distillation provided the impurities contained in it are themselves non-volatile. The apparatus used is shown in Fig. 8. The impure liquid is taken in a round-bottomed

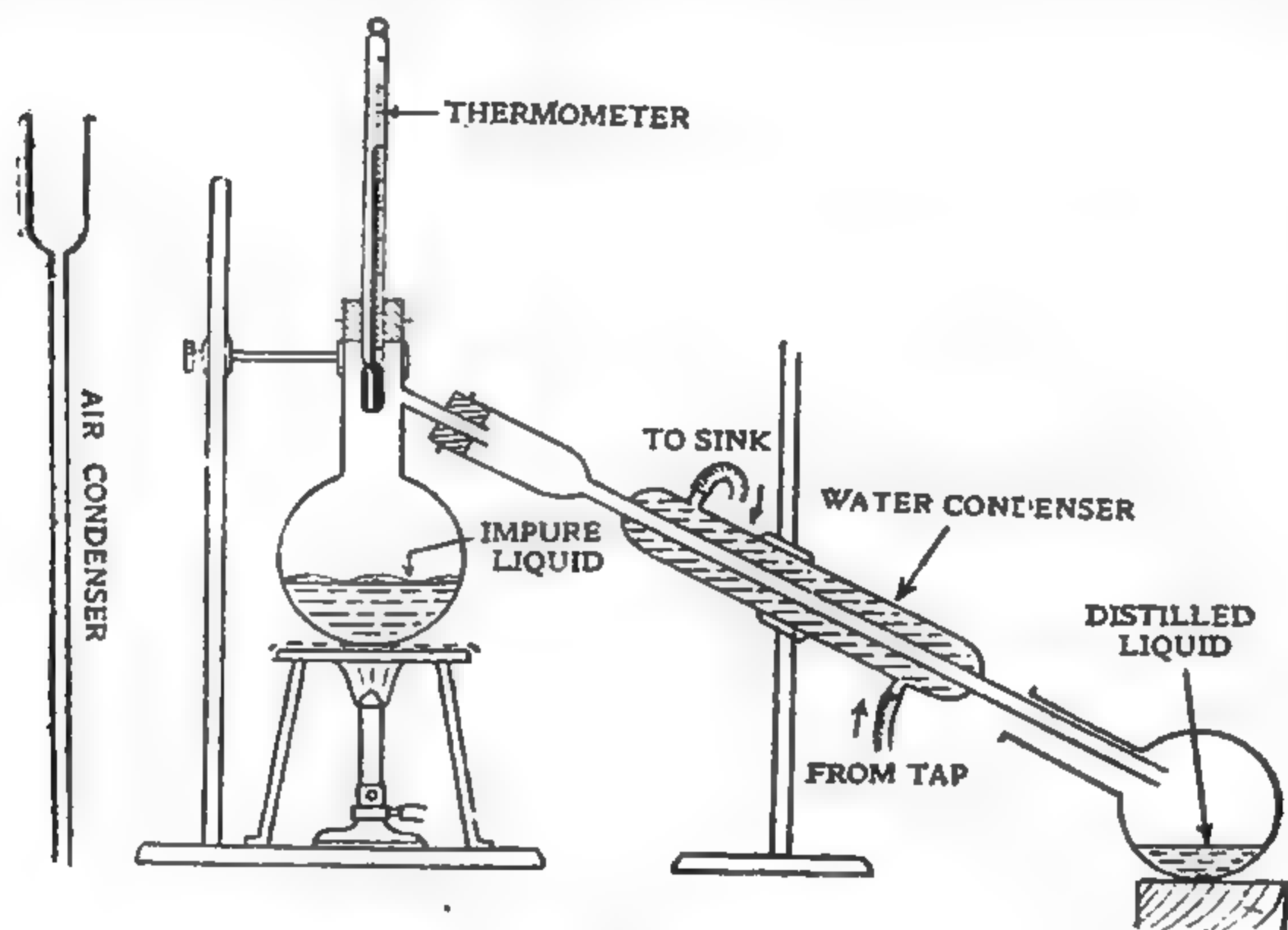


Fig. 8. Simple Distillation

Distillation flask having a side tube connected to a water condenser. The flask is heated directly on a flame. But if the liquid is inflammable, it is heated on a sand bath or a water bath. The vapour of the liquid pass through the condenser where they change into liquid which flows down into a receiver as shown in the figure. The impurities remain behind in the distillation flask.

To avoid superheating and bumping it is desirable to add a few pieces of unglazed porcelain or a few glass beads to the mixture in the distillation flask.

An important point to be remembered in the distillation process is that the thermometer, if used, should be kept above the liquid, just below the position where the side tube is fused into the neck of the flask, as shown in the figure.

5. Distillation Under Reduced Pressure. If the liquid to be purified is liable to decompose when heated to its boiling point in the ordinary way, under atmospheric pressure, the distillation can be carried out without decomposition at a much lower temperature under reduced pressure. As the chances of superheating and 'bumping' are greatly increased in distillation under reduced pressure, a special form of distillation flask, known as Claisen flask, is used to minimise this effect.

A simple form of low-pressure distillation apparatus is shown in Fig. 9.

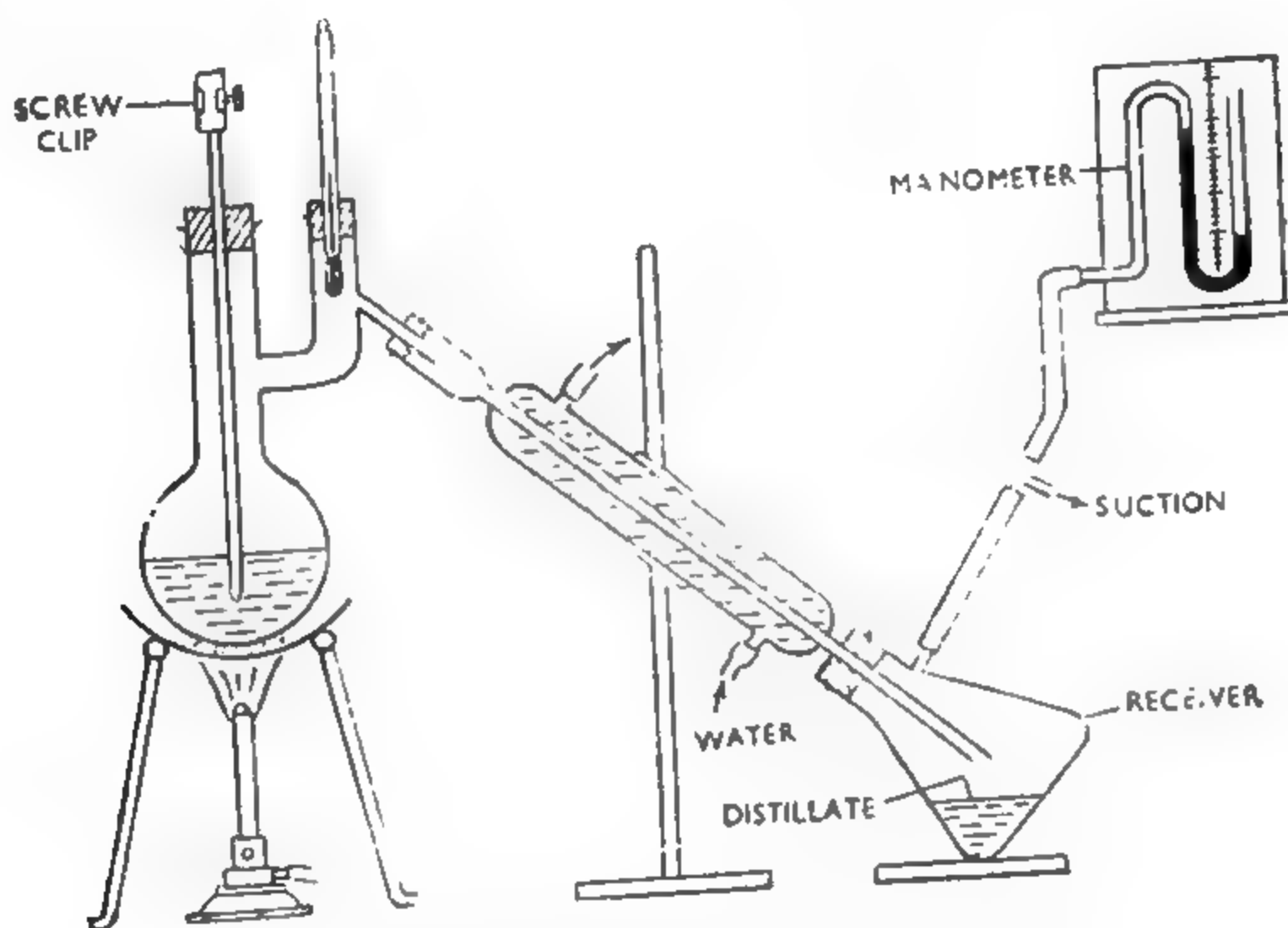


Fig. 9. Distillation Under Reduced Pressure.

The Claisen flask has two necks, one of which carries a thermometer as usual and the other carries a capillary tube which is partially closed from the above by a pressure tubing-screw clip arrangement through which a steady stream of air can be regulated. This avoids superheating. The side arm of the Claisen flask is then connected to a water-cooled condenser as usual. The pressure inside the apparatus is reduced by a filter pump or for lower pressures, by a vacuum pump. A mercury manometer to indicate the pressure, at which the distillation is being carried out, is often included in the assembly, as shown.

Thus glycerine, which has a normal boiling point of 290° , can be distilled without decomposition at 180° when the pressure is reduced to 12 mm.

6. Steam Distillation. This process consists in distilling a substance in a current of steam. It is applicable when the substance to be distilled (purified)

- (i) is insoluble in water
- (ii) has a high molecular weight
- (iii) has a fairly high vapour pressure at 100° , and
- (iv) the impurities contained in it are non-volatile.

The apparatus is shown in Fig. 10. The steam is generated in a metal can. The solution to be distilled is placed in the round-bottomed flask, clamped at an angle so as to prevent the solution from being splashed into the condenser. The tube carrying the steam from the can dips below the liquid in the flask. The distillation flask is kept heated gently on a sand bath in order to avoid too much condensation of water into it.

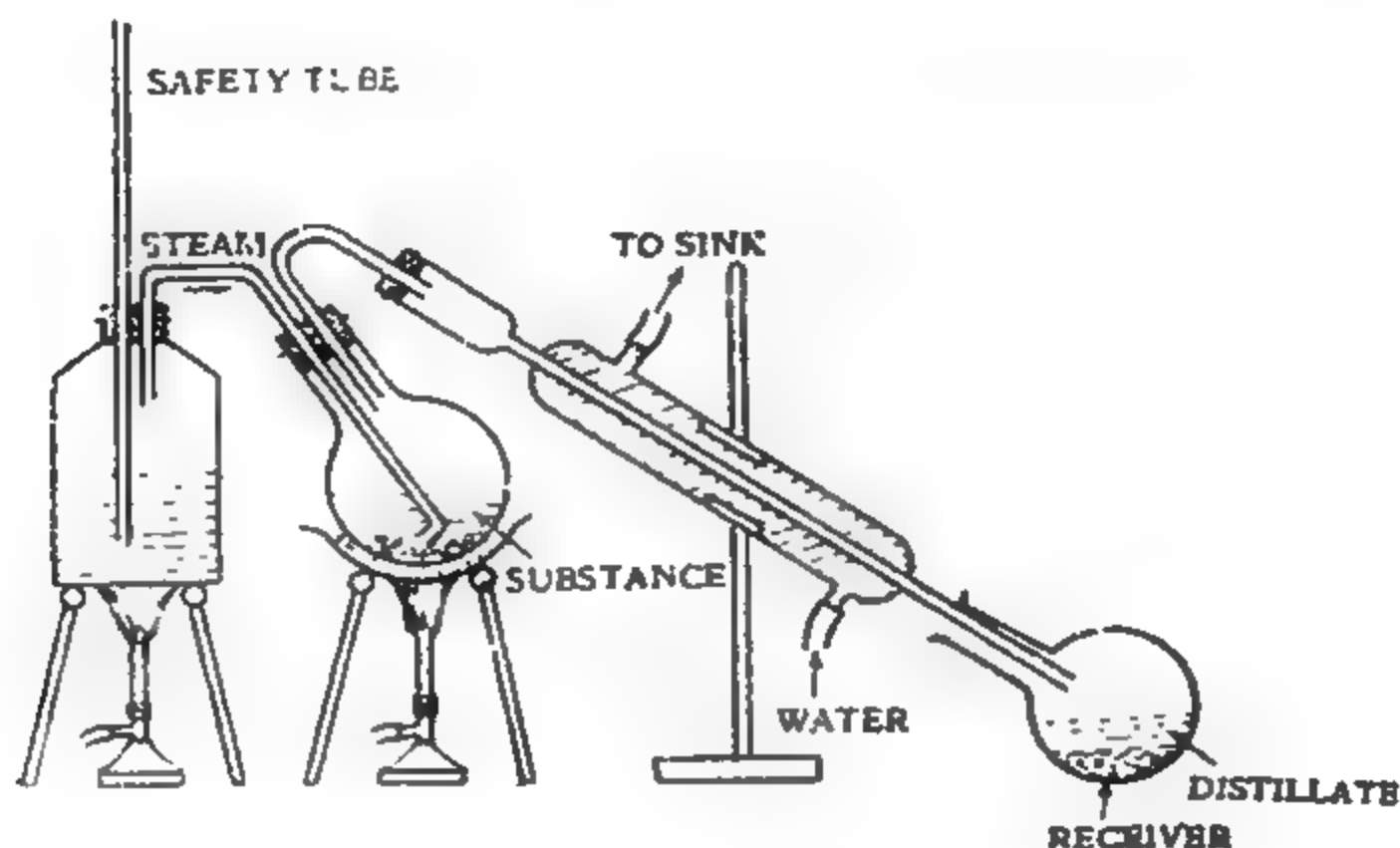


Fig. 10. Steam distillation

The boiling of the liquid in the flask soon sets in and the vapours of the organic compound mixed with steam pass over and are condensed in the receiver.

The next step is to separate the organic compound from water. If it is a solid, it may be separated by decantation or filtration. If it is a liquid, it can be isolated by putting the mixture in a separating funnel in the usual way.

Principle of steam distillation. It is well-known that a liquid boils at a temperature at which its vapour pressure becomes equal to the atmospheric pressure. Now, in steam distillation there are vapours of water as well as of the organic liquid (under distillation). Let p_1 be the vapour pressure of water and p_2 that of liquid. Evidently, the mixture will boil at the temperature at which

$$p_1 + p_2 = \text{atmospheric pressure.}$$

It is obvious that this temperature will be lower than the normal boiling point of the organic liquid or even of water because $p_1 + p_2$ can approach the atmospheric pressure sooner than either p_1 or p_2 alone. For example, aniline which boils normally at 184° will boil in steam at 98.5° (i.e., at a temperature which is even below the normal boiling point of water). Vapour pressure of water, p_1 , at 98.5° is 717 mm. and that of aniline, p_2 , is 43 mm.

$$\therefore p_1 + p_2 = 760 \text{ mm.} = \text{atmospheric pressure}$$

The relative amounts of aniline and water in the distillate depend upon molecular weights and vapour pressures at the boiling temperature.

Thus,

$$\frac{\text{weight of water distilled}}{\text{weight of aniline distilled}} = \frac{18 \times 717}{93 \times 43} = 3.23$$

7. Fractional Distillation. This method is used when two or more liquids with boiling points far removed from one another have to be separated.

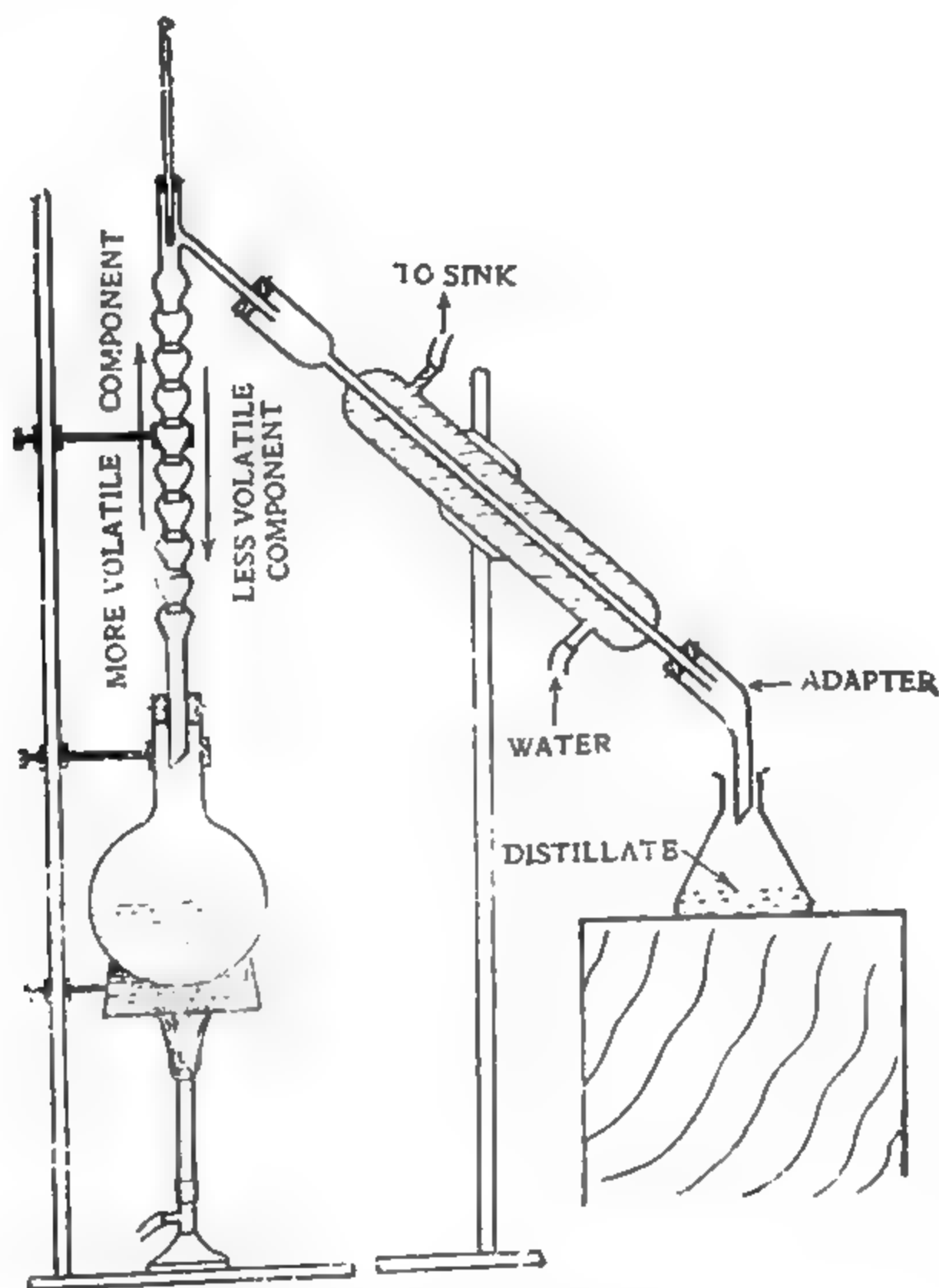


Fig. 11. Fractional distillation

If the liquids differ appreciably in their boiling points, say by 30 or 40°, they can be separated by using ordinary distillation apparatus shown in Fig. 8. Suppose one liquid (*A*) boils at 50° and the second liquid (*B*) boils at 90°. Then on heating their mixture in the distillation flask, the fraction boiling in the neighbourhood of 50° will contain mostly *A* together with a small amount of *B* while the fraction boiling in the neighbourhood of 90° will contain mostly *B* together with a small amount of *A*. These fractions are separately collected and then redistilled two or three times. Ultimately, the fraction collected at 50° will be pure *A* and that collected at 90° will be pure *B*.

It may be recalled that the boiling point of a liquid or the mixture of two or more miscible liquids, is the temperature at which the vapour pressure becomes equal to the atmospheric pressure. Now, as the more volatile component (*A*) starts distilling over at about 50° , the liquid phase becomes richer in the less volatile liquid *B*. The vapour pressure will, therefore, decrease. In order to bring the vapour pressure again at the level of atmospheric pressure so as to keep the mixture boiling, the temperature will have to rise. Thus there is almost a continuous rise in temperature with continued boiling, although the rate of rise is less rapid near the first boiling. The students are cautioned against the common mistake in certain texts that the temperature remains constant at the first boiling point till the whole of the low boiling component distils over and then rises all of a sudden to the next boiling. This statement is contrary to theory as well as practice.

When the liquids to be separated have very close boiling points, such as acetone (B.P. 56°) and methyl alcohol (B.P. 65°), a fractionating column is fitted into the distillation flask (Fig. 11).

A fractionating column is a long tube of wide bore blown into a series of bulbs either spherical or pear-shaped. Alternatively, the tube is

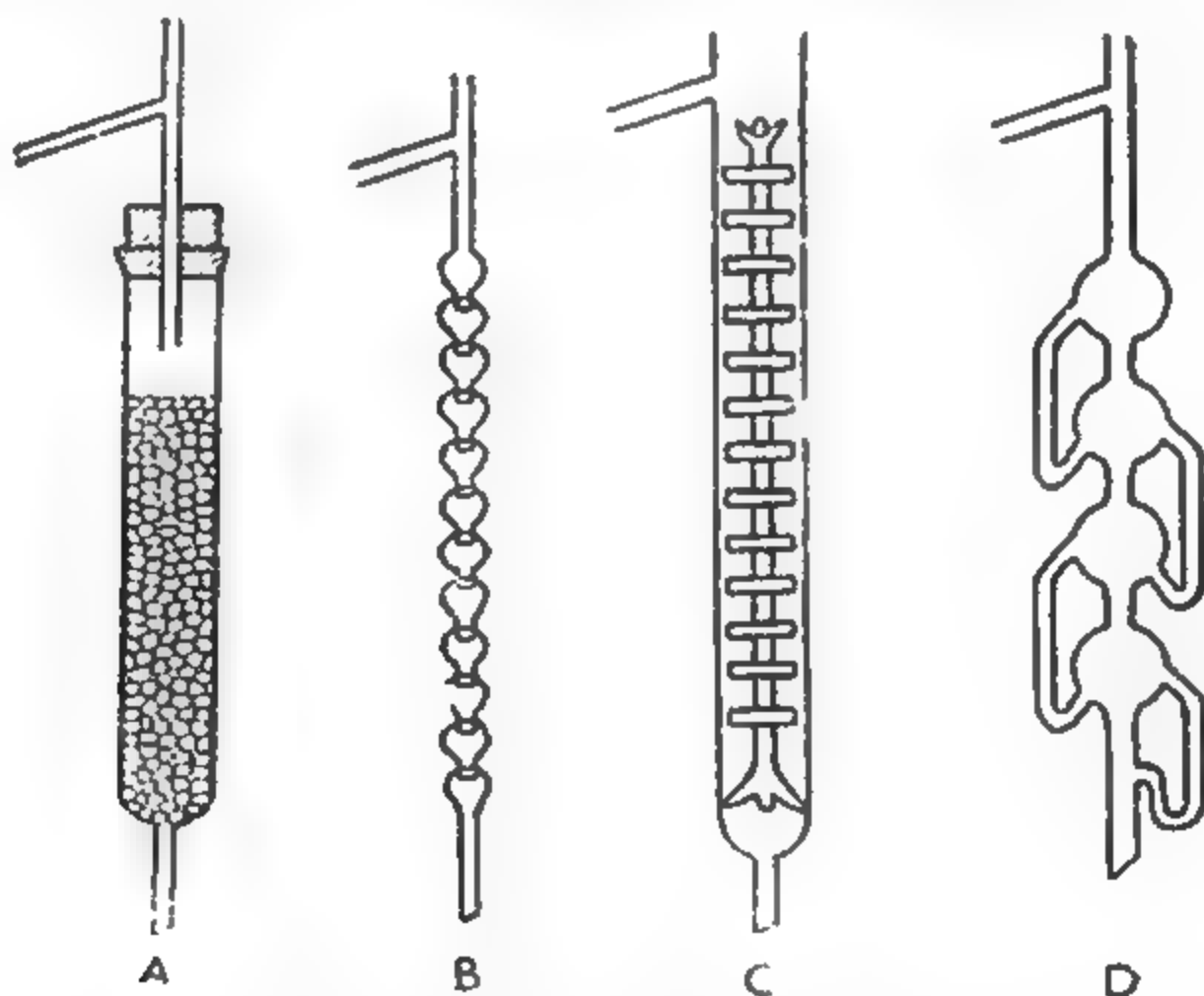


Fig. 12. Fractionating columns.

filled with glass beads or broken glass tubes. The real purpose is to increase the cooling surface and to provide obstruction to the passage of ascending vapour or descending liquid. Several types of fractionating columns are used in laboratory operations as well as in industrial processes. Some of the fractionating columns commonly used in laboratory operations are shown in Fig. 12. Out of these, two forms shown as *A* and *B*, have been found to be more useful than the rest. The form *A* consisting of a glass tube packed with very small pieces of glass tubing or glass beads is probably the most effective.

In industrial processes much longer columns are used.

The principle of a fractionating column will be clear from the following. As the mixture containing liquids *A* and *B* boiling, say at 55° and 65°C respectively, is heated in the distillation flask (Fig. 11), the

vapours consisting more of *A* than of *B* rise up. On coming into contact with the large cooling surface of the fractionating column, the vapour of *B* condense while those of *A* pass over and collect into the receiver. As the condensate (liquid) consisting mostly of the less volatile component *B* flows down the fractionating column, it meets the fresh hot ascending vapours. During this meeting process the ascending vapours are robbed off the less volatile component *B* which condenses and joins the downward flowing liquid while the condensate (liquid) loses its more volatile component *A* which joins the upward going vapours now very much enriched in *A*. This process is repeated at every point in the fractionating column with the result that by the time the vapours reach the top of the column they consist mainly of component *A* while the down flowing liquid contains mostly the component *B*. In this way an almost complete separation is effected in two or three operations.

CRITERIA OF PURITY

There are a number of methods of ascertaining the purity of organic compounds. Amongst these, melting point and boiling point determinations for solids and liquids respectively are the simplest and most reliable. The other methods include density, refractive index and viscosity measurements.

Melting point. The most reliable method for testing the purity of a solid compound is the determination of its melting point. A pure compound will always melt sharply within a range of less than 1° whereas an impure compound will melt over a wide range of temperature. Moreover, a pure compound will always melt at a fixed temperature under ordinary conditions whereas an impure compound will melt at an indefinite temperature. The apparatus commonly employed for determining melting point is shown in Fig. 13. The substance is dried and powdered and a small amount of it is taken in a capillary tube about 6–7 cm. long and 1 mm. diameter with one end sealed. The substance added should be sufficient to fill 1 cm. or so of the capillary tube. The capillary tube is then slightly moistened and held to a thermometer and lowered in a water bath or sulphuric acid bath depending upon the fact whether the melting point of the substance is expected to be below or above 100° respectively. It is important that the bottom of the capillary tube where the substance is located should lie opposite to the thermometer bulb and about half of the capillary tube should stand above the surface of the liquid. The bath is provided with a stirrer as shown.

The liquid bath is heated very slowly with gentle stirring. As the melting point approaches, the opaque solid is seen to become a transparent liquid. The temperature recorded on the thermometer gives the melting point. If the value agrees with known melting point of the compound, the substance under examination may be taken as pure.

If, however, the melting point is not known, the substance may be recrystallised and the melting point determination repeated. If the two values agree, the substance is pure.

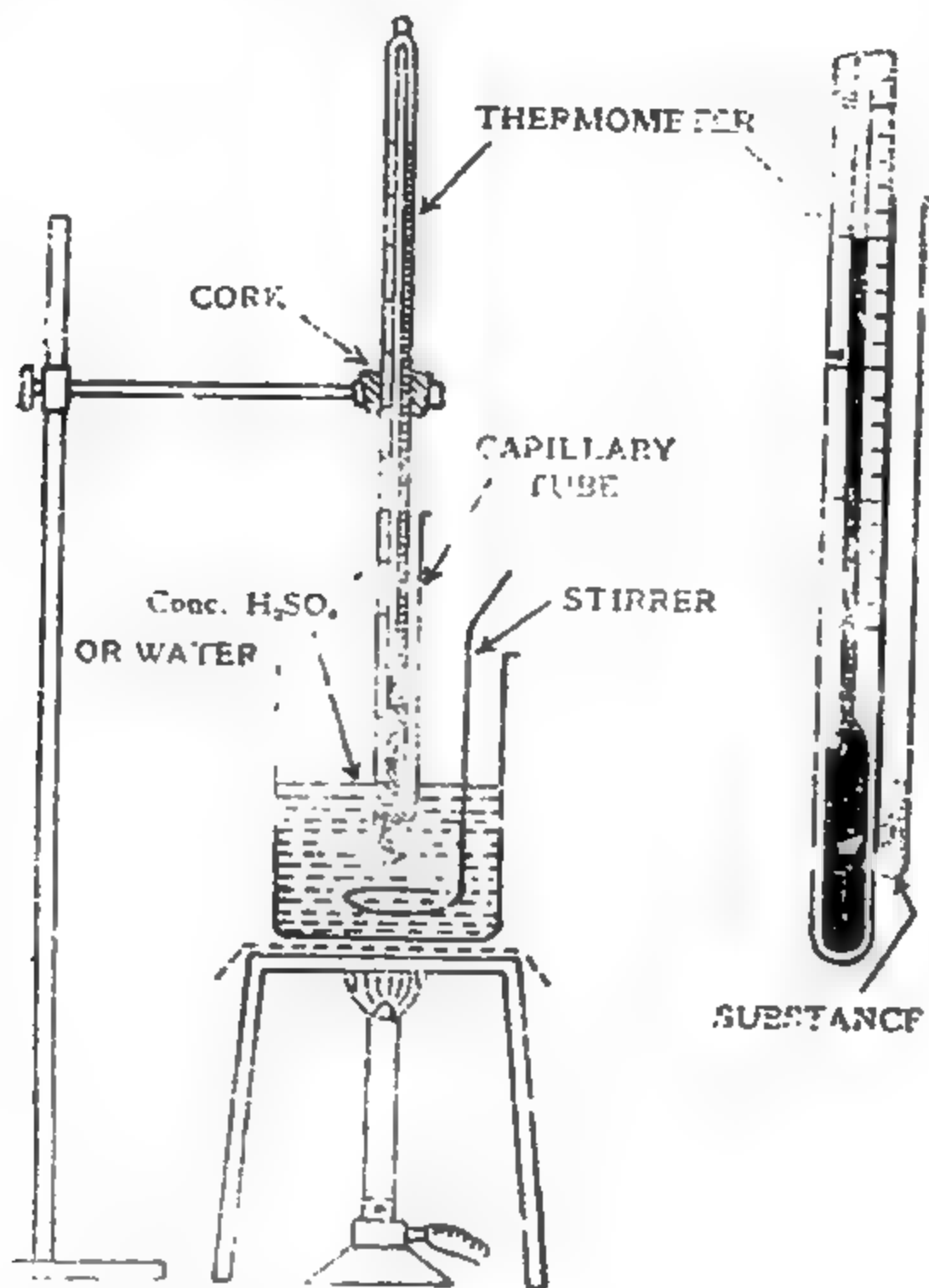


Fig. 13. Determination of melting point

Mixed Melting Point. The identification of a compound can be confirmed by the method of *mixed melting point*. Suppose the compound, the melting point of which has been determined, is believed to be X. Some of it is mixed with a little of pure compound Y and the melting point of the mixture determined. If the melting point is unchanged then the original compound is X. If the melting point is less, the compound is not X.

Boiling Point. If the compound under examination is a liquid, its purity can be established by determining its boiling point. One simple method of determining boiling point if the liquid is present in a sufficient quantity, is to distil it as in the apparatus shown in Fig. 8. If the temperature recorded on the thermometer held just below the side tube remains the same throughout, the liquid is pure. However, if the temperature rises during the distillation, the inference is that the liquid is associated with some impurities.

If the amount of the liquid available is small, an alternative procedure known as **Siwoloff's method** is used. A small quantity of the liquid is taken in a thin-walled test tube and a capillary tube sealed at about one

centimetre from one end is introduced into it. The test tube is then attached to a thermometer by means of a rubber band in such a way that the liquid stands just by the side of the bulb as shown in Fig. 3 14. This assembly is lowered into a beaker containing water or sulphuric acid or any other suitable liquid. The bath is heated gently and the liquid stirred slowly but continuously. At first a few bubbles will be seen to rise from the lower end of the capillary but their number becomes more and more as the temperature rises. When the boiling point of the liquid is reached the bubbles rise in a rapid stream in quick succession. This temperature is noted. The stirring is continued but heating is stopped and the

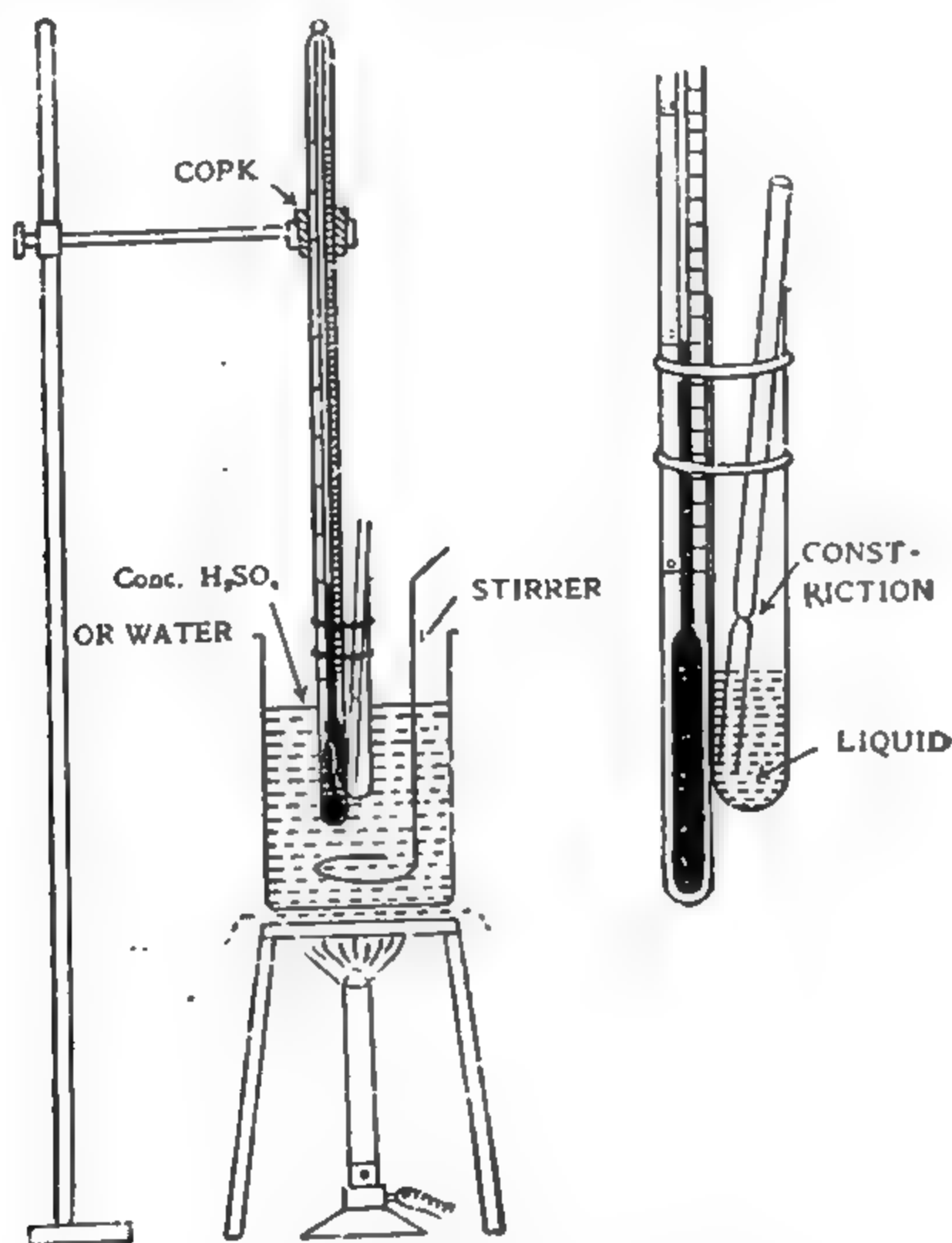


Fig. 14. Determination of Boiling Point

temperature at which the evolution of the bubbles just ceases is noted. The mean of the two temperatures gives the boiling point of the liquid.

Mixed Boiling Point. The identification of a liquid can be confirmed by the method of mixed boiling point. Suppose the liquid whose boiling point has been determined, is believed to be *X*. Some of it is mixed with a little of pure compound *X* and the boiling point of the mixture determined. If the boiling point is unchanged, then the original liquid is *X*. If the boiling point is raised, the compound is not *X*.

QUESTIONS

1. Outline briefly the various methods in vogue for the purification of solid organic compounds. Discuss their relative merits and demerits.
2. Explain why it is necessary to distil organic liquid sometime under a reduced pressure. Describe one such method.
3. What is fractional distillation? Is it possible to separate two miscible liquids from one another by fractional distillation in a single process?
4. What is a fractionating column? How is it possible to get a better separation of miscible liquids by means of a fractionating column?
5. How would you find whether a given solid is pure or not? If it is impure, how would you purify it?
6. How would you ascertain whether a given liquid is pure or not? If it is impure, how would you purify it?
7. Discuss the principle of steam distillation. How is aniline purified by this method?
8. Explain how would you effect the separation of two liquids with boiling points separated from each other, say, by 10°C .
9. Write notes on the following :

(i) Soxhlet extraction	(ii) Fractional distillation
(iii) Vacuum distillation	(iv) Steam distillation.
10. How would you determine (a) the boiling point of a liquid (b) the melting point of a solid if they are available in small quantities?
11. Explain so far as possible, with examples, any three of the following for purifying an organic substance :

(i) Fractional distillation	(ii) Steam distillation	(iii) Vacuum distillation	(iv) Crystallisation
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 (v) Extraction with a solvent. How would you ascertain that the sample obtained is pure?
(Panjab Inter. 1962 S)
12. You are given a mixture of aniline and caustic soda solution. Describe giving details, how would you get a pure sample of aniline. Explain the principle underlying the various operations. How would you prove that the sample got is actually pure?
(Panjab Inter. 1954)
13. Name and explain the process involved in the separation of a pure organic compound from the following types of mixtures :
 - (i) Of two soluble substances but with different solubilities.
 - (ii) Of two volatile liquids but with boiling points not far removed from each other.
 - (iii) Of an organic liquid and an inorganic miscible impurity.
14. Draw a neat sketch of the apparatus used in the process of steam distillation and explain its working. Name one organic liquid which though immiscible with water is volatile in steam. Enumerate the criteria of purity of an organic compound.
(Panjab Inter. 1956 S)
15. Describe how you would separate into its components a mixture of liquid organic compounds. If some of the liquids are decomposed by strong heating, what modification would you make in the process. Illustrate your answer by simple diagrams.
(Panjab Inter 1957 S)
16. In the preparation of a liquid organic compound, the product obtained is mixed with about ten times its volume of strong aqueous solution of inorganic salts. What methods would you try for isolation of the organic liquid?
(Panjab Inter. 1958)

17. Write notes on fractional distillation and distillation under reduced pressure. Indicate the special significance of these methods. Draw a diagram illustrating each of the operations. (U.P. Inter 1962)

18. Describe in detail the various methods employed in purifying organic compounds. Show how you would test that the compound prepared is pure. (Panjab Inter. 1962)

19. Describe the process of crystallisation, distillation and sublimation. Mention their importance in organic chemistry. How can you know whether an organic compound, solid or liquid, is pure? (Delhi Hr. Sec. 1955)

20. Describe the various methods employed in purifying the organic compounds. How would you test that the compound prepared by you is pure? (Jammu and Kashmir Inter. 1956)

21. Fill in the blanks :

- Crystallisation is a process for — of —.
- The criteria of purity are — and — for — and — respectively.
- A compound which is volatile in steam can be purified by —.
- Vacuum distillation is used for such compounds as — before their — is reached.
- Sublimation is used for purifying — which are — and are contaminated with — impurity.

22. You are given a mixture of aniline and KOH solution. How will you get pure aniline from it? (Panjab T.D.C. Part I 1963)

23. Explain briefly with the help of diagrams any three of the following :

- Fractional distillation.
- Vacuum distillation.
- Steam distillation.
- Extraction with a solvent.

(Panjab T.D.C. Part I, 1964)

24. (a) Draw a simple diagram of the apparatus used in the following operations :

- Fractional Distillation.
- Distillation under reduced pressure.

(b) You are given a solid sample of a known organic compound. How will you find out whether the compound is pure or not. (Panjab T.D.C. (I) 1966)

CHAPTER XIX

DETECTION OF COMMON ELEMENTS

The common elements which occur in organic compounds are few in number, being generally carbon, hydrogen, oxygen, nitrogen, the halogens, sulphur, phosphorus and sometimes metals. A specific test for each element, except oxygen, has been standardised. The presence of oxygen is inferred from certain characteristic reactions of oxygen-containing groups such as $-\text{OH}$, $-\text{CHO}$, $>\text{C}=\text{O}$, $-\text{COOH}$, etc.

Detection of Carbon and Hydrogen. The presence of carbon in an organic compound is assumed. However, the presence of carbon can be

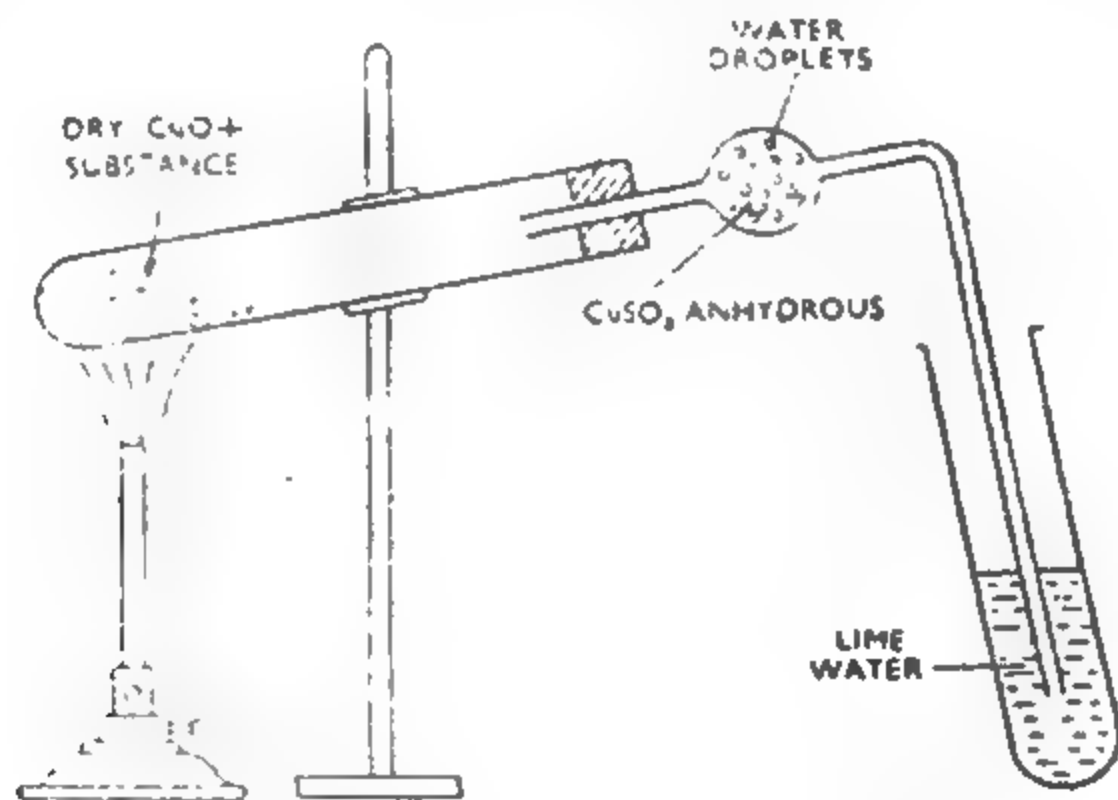


Fig. 1. Detection of Carbon and Hydrogen.

tested along with hydrogen. A small amount, about 0.1 gm., of the powdered substance is mixed with about ten times its weight of finely powdered and dried copper oxide and the mixture is heated in a hard glass test tube provided with a delivery tube which is dipping in lime water as shown in Fig. 1. The presence of hydrogen is indicated by the condensation of water in the bulb and that of carbon by milky development in the lime water due to the formation of sparingly soluble calcium carbonate. The condensed water is tested by anhydrous copper sulphate.

Precaution. The copper oxide used in this test must be completely dry otherwise a small amount of the moisture contained in it may give

DETECTION OF COMMON ELEMENTS

a mist on the upper surface of the reaction tube giving a wrong indication of the presence of hydrogen. The test tube should also be dry for obvious reasons.

Detection of Nitrogen (a) Soda lime test. An easy, though not dependable, test for nitrogen consists in heating the substance (liquid or solid) with soda lime and testing for ammonia in the issuing gases. The test is of no value if negative results are obtained because a number of nitrogenous compounds (such as nitro- and diazo derivatives) do not yield ammonia under these conditions.

(b) Lassaigue's test. A small pellet of metallic sodium is heated gently in a fusion tube (a small test tube of soft glass), as shown in Fig. 2. When it is melted, a small amount of the substance is added and heating continued first gently and then as strongly as possible. The red hot tube is plunged into a small amount of distilled water contained in a china dish and thereby broken. The fused mass passes into water along with pieces of the broken fusion tube. The suspension is boiled for a couple of minutes and then cooled and filtered. The filtrate obtained is usually alkaline. If it is not, it should be made alkaline by the addition of a drop or two of a dilute solution of sodium hydroxide.

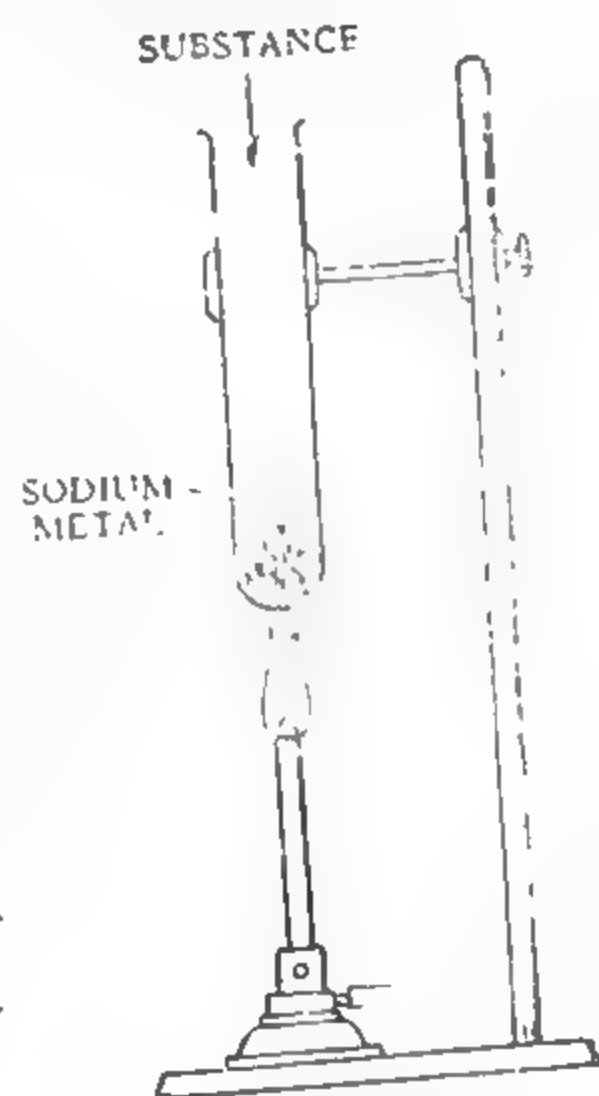


Fig. 2. Fusion with sodium metal.

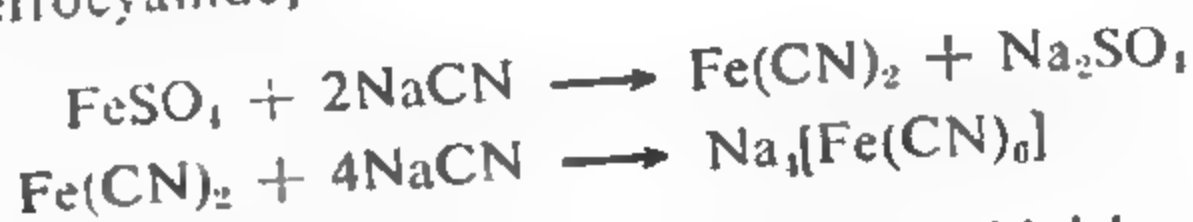
To a part of the filtrate is added a small amount of the freshly prepared solution of ferrous sulphate and the mixture is warmed. A few drops of ferric chloride solution are then added and the solution is acidified with hydrochloric acid. If nitrogen is present in the original compound, a bluish green or blue colouration is obtained.

The reactions taking place in the Lassaigue's test are explained below :

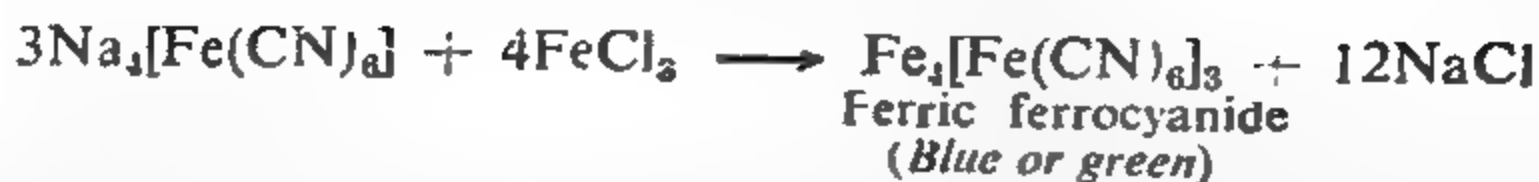
When the organic substance is fused with sodium, the nitrogen (if present) and carbon of the compound form sodium cyanide :



The solution is usually alkaline as a very small excess of sodium is generally left which reacts with water to form sodium hydroxide. The reaction of the alkaline solution with ferrous sulphate leads to the formation of sodium ferrocyanide,



which then reacts with ferric chloride to give blue (or bluish green) ferric ferrocyanide.



The addition of hydrochloric acid is necessary to dissolve any ferrous hydroxide that may be formed by the action of sodium hydroxide on ferrous sulphate. If this is not done, *green* precipitate of $\text{Fe}(\text{OH})_2$ might cause confusion giving wrong indication for the presence of nitrogen.

If the substance contains both nitrogen and sulphur, sodium sulphocyanide may be formed which with ferric chloride will give a blood red colour due to the formation of ferric sulphocyanide.



If the organic compound is a volatile liquid, it may simply boil off without reacting with sodium. In such cases the fusion tube should be much longer so that a part of the substance may condense in the upper cooler part and fall back to come in contact with the molten sodium.

Detection of the Halogens. (a) **Beilstein's test.** A piece of copper wire with a flattened end is cleaned and heated in an oxidising flame till it no longer emits green colour. It is then dipped into the substance and brought back into the flame. If the green or blue colour re-appears, the presence of the halogens (chlorine, bromine or iodine) is indicated. This is not a very reliable test as a few substances such as urea, thiourea, containing no halogens, also give positive test thus misleading the worker.

(b) **Lassaigne's test.** A small amount of the substance is heated with metallic sodium as in the test for nitrogen when the halogen present will combine with sodium giving the corresponding halide (NaX). The fused mass is extracted with water and filtered. The filtrate is acidified with nitric acid and boiled to decompose the cyanide or sulphide, if any. This solution is cooled and a small amount of silver nitrate solution is added to it. If any of the halogens is present, a precipitate will be obtained.



White precipitate (of AgCl) soluble in ammonia and insoluble in nitric acid will indicate the presence of chlorine; pale yellow precipitate (of AgBr) only partly soluble in ammonia but insoluble in nitric acid will indicate the presence of bromine while a yellow precipitate (of AgI) insoluble in ammonia as well as in nitric acid will show the presence of iodine in the compound.

The presence of bromine or iodine can be further confirmed by taking a portion of the Lassaigne's filtrate, boiling with nitric acid as before, adding a few ml. of carbon tetrachloride and a small amount of freshly prepared chlorine water. On allowing to stand, the carbon tetrachloride layer will turn orange if bromine is present and violet if iodine is present in the compound.

Detection of Sulphur. The Lassaigne's filtrate is obtained as in the preceding tests. If the compound contains sulphur, sodium sulphide will be obtained in solution.



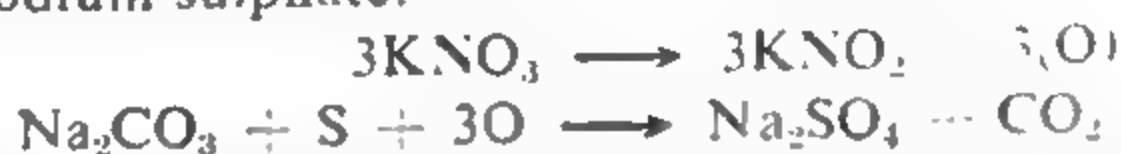
The presence of sodium sulphide can be detected by any of the following tests :

(i) By the addition of sodium nitroprusside, a deep violet coloration is obtained.

(ii) By the addition of lead acetate and acetic acid, a black precipitate of lead sulphide is obtained.



If a substance is too volatile, it may not respond to the above test for sulphur. In such cases the compound is fused with a mixture of potassium nitrate and sodium carbonate, when sulphur, if present is oxidised to sodium sulphate.



The presence of sodium sulphate in solution is detected by the addition of barium chloride when a thick white precipitate of barium sulphate insoluble in all acids is obtained.



Middleton's test for N, S, and halogens. More recently a new method, known as **Middleton's method** has come into vogue. In this method a small amount of the substance is thoroughly mixed with about 5 times its weight of a mixture of zinc dust and sodium carbonate (2 : 1) and strongly heated. The fused mass is extracted with distilled water and filtered. The filtrate is then treated exactly in the same way as in Lassaignes test for detection of nitrogen, sulphur and halogens.

This method is evidently simpler and more convenient than the Lassaigne's method and is used in many laboratories.

Detection of Phosphorus. The usual method of detecting phosphorus is to oxidise it to phosphoric acid. For this purpose, the substance is fused with sodium peroxide and the fused mass is extracted with water. The filtrate containing sodium phosphate is heated with concentrated nitric acid and ammonium molybdate. A yellow precipitate or colour (of ammonium phosphomolybdate) shows the presence of phosphorus in the original compound.

Detection of Metals. The substance is ignited on a platinum foil to destroy all organic matter. The residue is examined for metallic radicals by the usual qualitative analysis.

QUESTIONS

1. Describe and explain the tests used to detect nitrogen and chlorine in an organic compound,

2. How would you detect sulphur in an organic compound ?

3. Explain the following :

(i) While testing for halogens the Lassaigne's filtrate is boiled with nitric acid.

(ii) Beilstein's Test for halogens is not reliable.

(iii) Soda lime test for nitrogen is misleading.

(iv) Completely dry copper oxide is used in testing hydrogen.

4. What elements other than carbon are commonly present in organic compounds? Give tests for any two of them.

5. You are given a sample of para amino-benzene sulphonic acid (sulphanilic acid). How would you proceed to establish the presence of the different elements in it? (Panjab Inter. 1953)

6. Describe carefully how you would detect the presence of nitrogen in an organic compound and explain as far as possible the reactions involved by means of equations. (Panjab Inter. 1957)

7. Describe in detail the methods used for the detection of halogens in an organic compound. Give *equations* and *reasons* for the various operations. (Panjab Inter. 1958)

8. An organic compound contains N, S and Br. How would you proceed to determine the presence of the above elements in it? (Ajmer, Inter. 1952)

9. How would you detect the presence of N, P and Br in organic compound? (Bihar, Inter. 1959)

10. Describe how the presence of sulphur, nitrogen and chlorine in an organic compound can be detected. (Andhra Inter. 1962)

11. Give a scheme for the detection of nitrogen, sulphur and iodine in an organic compound giving equations for the reactions that take place at each step. (U.P. Inter. 1950)

12. Fill in the blanks :

(i) Lassaigne's test is used for—.

(ii) Beilstein's test is not a—test for halogens.

(iii) Oxygen is detected by—method only.

13. Describe the experimental details of Lassaigne's test for detection of N, S and halogens. Give equations to explain the chemistry of reaction in each case. (Panjab T.D.C. Part I, 1963)

CHAPTER XX

QUANTITATIVE ANALYSIS

After identifying the elements, the next step in the systematic investigation of an organic compound is to find out the percentage by weight of each element contained in it. The methods in use at present are capable of giving results of very high degree of accuracy.

Estimation of Carbon and Hydrogen. The method for estimating carbon and hydrogen rests on the principle that known weight of the *dry* substance is heated in a current of *dry* air (free of carbon dioxide) or *pure oxygen*, in the presence of *dry* copper oxide, till all the carbon is oxidised to carbon dioxide and all the hydrogen to water. The weight of carbon dioxide produced is determined by absorbing it in weighed potash bulbs and that of water by absorbing it in weighed calcium chloride tubes. This method is known as **Liebig's combustion method**.

Apparatus. The apparatus consists of three parts :

- (1) *Oxygen or air supply*
- (2) *Combustion tube*
- (3) *Absorption unit*

(1) **Oxygen or Air Supply.** The oxygen or air used is freed from moisture and carbon dioxide by passing it through a series of wash bottles or bubblers containing concentrated sulphuric acid and U-tubes containing soda lime (not shown in the diagram).

The gas is then led through a bubbler or a conical flask containing concentrated sulphuric acid (Fig. 2.) This serves as a gauge to indicate the rate of flow of the gas.

(2) **Combustion Tube.** The combustion tube is made of pyrex glass or of silica and is open at both ends. It is about 2 cm. in diameter. Its length is about 10 cm. more than the furnace in which it is to be heated. As the length of the furnace usually varies from 75 to 80 cm., the length of the combustion tube varies from 85 to 90 cm. The ends of the tube are fitted with rubber corks singly bored. Air or oxygen enters from one end and the gases produced during the combustion leave at the other end.

The tube is filled as shown in Fig. 1.

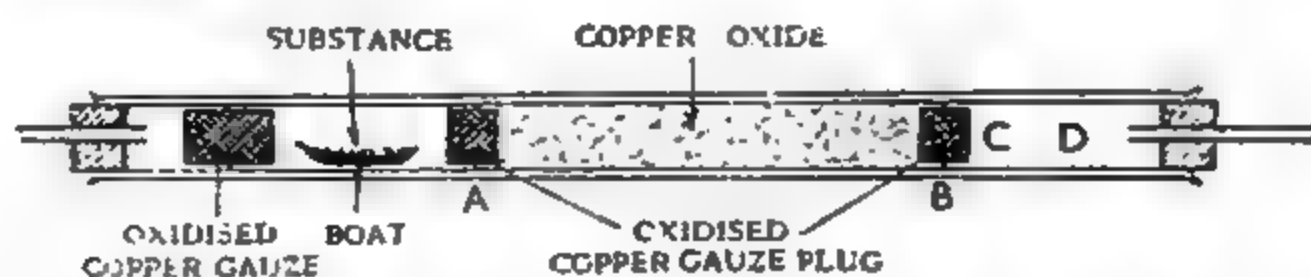


Fig. 1. Filling of combustion tube in the estimation of carbon and hydrogen.

About half of the tube is filled with dry ignited copper oxide held in position by two oxidised copper gauze plugs *A* and *B*. About 0.2 gm. of the organic compound under examination, accurately weighed, is placed in a small porcelain boat. Next, to the left, is put an oxidised copper role occupying nearly 15 cm. of the tube.

(3) **Absorption Unit.** The absorption unit (Fig. 2.) consists of three parts which can be detached from one another :

(a) *A weighed calcium chloride U-tube* to absorb water produced during the combustion.

(b) *Weighed potash bulbs*, more than half filled with concentrated potassium hydroxide solution, to absorb carbon dioxide produced during combustion and

(c) *A guard tube* containing a mixture of fused soda lime and calcium chloride to prevent the entry of moisture and carbon dioxide from the atmosphere into the potash bulbs.

Procedure. In the beginning, before placing the organic substance in the boat, the absorption unit is disconnected from the combustion tube. The tube is heated strongly by lighting all the burners so as to dry it completely. A slow current of dry air or oxygen freed from carbon dioxide, is also passed through it to facilitate the *complete removal of moisture and carbon dioxide from the tube*. This continues for about twenty minutes.

About 0.2 gm. of the substance to be analysed is accurately weighed in the boat which is introduced into the combustion tube. The calcium

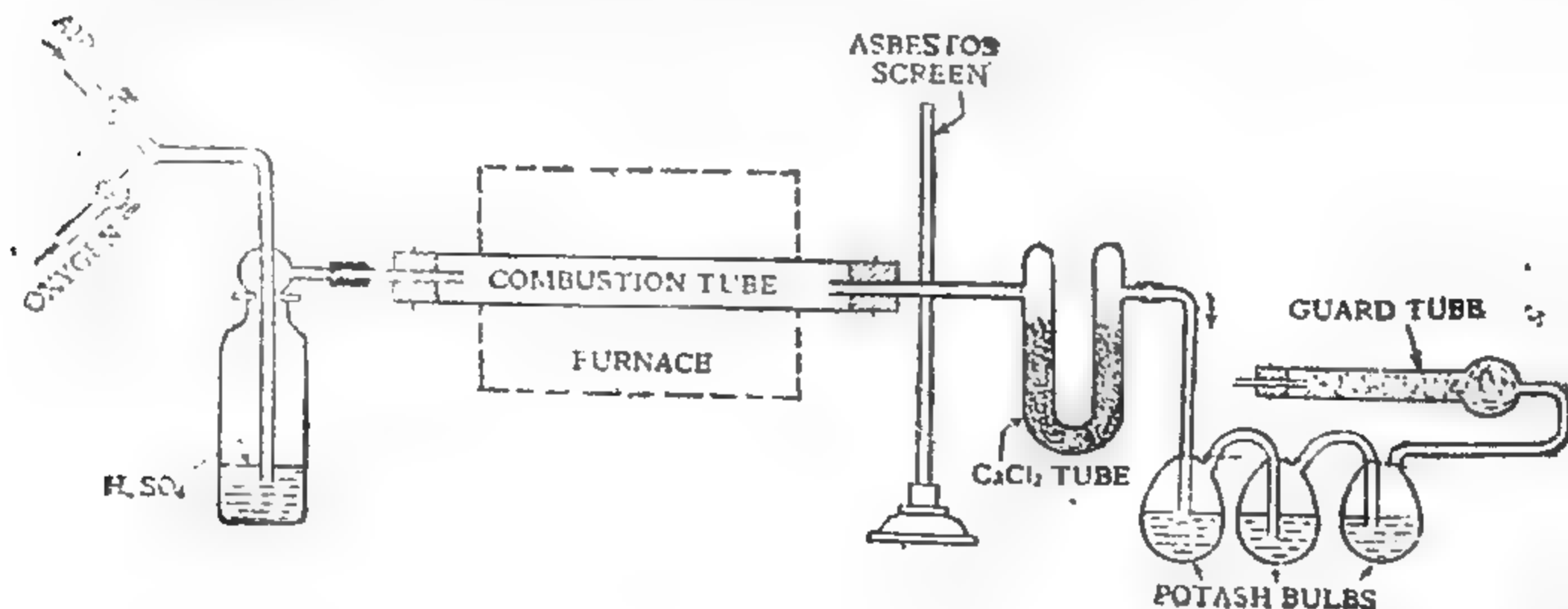
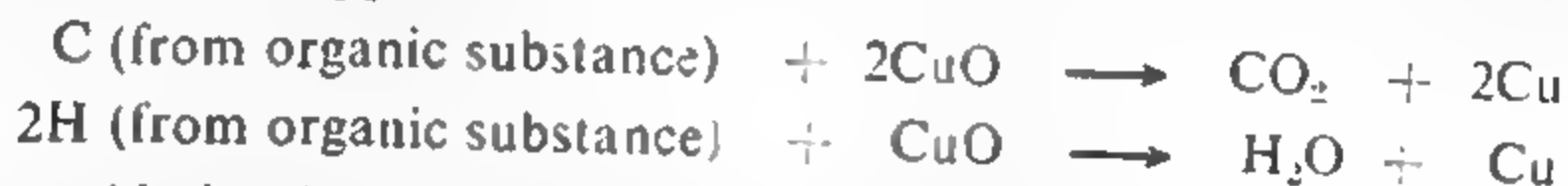


Fig. 2. Apparatus for the estimation of carbon and hydrogen.

chloride tube and the potash bulbs of the absorption unit are also accurately weighed and connected in the assembly, as shown in Fig. 2. All connections must be air-tight.

At first, a slow stream of air or oxygen is led through the tube and the copper oxide layer is heated by lighting all the burners beneath it. Ultimately the boat itself is heated by lighting the burners below it. The organic substance is strongly volatilized and the carbon and hydrogen present in it are oxidised to carbon dioxide and water respectively by interaction with copper oxide.



The oxidation is aided by the current of air or oxygen. *The oxidised copper gauze, placed to the left of the boat, serves to oxidise any vapour of the substance which may diffuse backwards.*

The heating is continued till the whole of the substance is completely oxidised. It usually takes from two to three hours for complete combustion. Towards the end, the current of air or oxygen is made more rapid to ensure the complete sweeping away of all traces of carbon dioxide and moisture produced. The absorption assembly is then disconnected. When cooled, the calcium chloride tube and the potash bulbs are separately weighed to find out the amount of water and carbon dioxide formed.

Precautions. If the organic compound contains nitrogen also, it may be partially oxidised to oxides of nitrogen. As they are also soluble in potash solution, they introduce an error. Therefore, a roll of bright copper gauze is put into the combustion tube at C (Fig. 1). This reduces the oxides of nitrogen back to nitrogen and the error is avoided.

If the organic compound contains halogens, it is advisable to put a roll of silver gauze at D. It absorbs any free halogen forming the silver halide.

If the substance contains sulphur, the copper oxide used is mixed with lead chromate which will retain the sulphur as lead sulphate.

Calculations.

Let the weight of the substance = w gm.

Increase in the weight of calcium chloride tube

i.e., the weight of water formed = x gm.

Increase in the weight of potash bulbs, *i.e.*, the

weight of carbon dioxide formed = y gm.

44 gm. of $\text{CO}_2 \equiv 12$ gm. of carbon

$$\therefore \text{Percentage of carbon} = \frac{12}{44} \cdot y \cdot \frac{100}{w}$$

18 gm. of $\text{H}_2\text{O} \equiv 2$ gm. of hydrogen

$$\therefore \text{Percentage of hydrogen} = \frac{2}{18} \cdot x \cdot \frac{100}{w}$$

Example 1. 0.280 gm. of an organic compound containing carbon, hydrogen and oxygen gave on combustion 0.3933 gm. of carbon dioxide and 0.1693 gm. of water. Calculate the percentage of carbon and hydrogen.

Weight of the substance = 0.280 gm.

Weight of carbon dioxide = 0.3933 gm.

Weight of water = 0.1693 gm.

∴ Wt. of carbon in 0.280 gm. of the substance

$$= \frac{12}{44} \times 0.3933$$

$$\begin{aligned} \therefore \text{Percentage of carbon} &= \frac{12}{44} \times \frac{0.3933}{0.280} \times 100 \\ &= 38.30 \end{aligned}$$

Similarly, weight of hydrogen in 0.280 gm. of the substance

$$= \frac{2}{18} \times 0.1693$$

$$\begin{aligned} \therefore \text{Percentage of hydrogen} &= \frac{2}{18} \times \frac{0.1693}{0.280} \times 100 \\ &= 6.72 \end{aligned}$$

Example 2. An organic substance contains carbon, hydrogen and oxygen. 0.24 gm. of the substance gave on combustion 0.036 gm. of water and 0.22 gm. of carbon dioxide. Calculate the percentage composition of the compound.

Weight of the substance = 0.24 gm.

Weight of water = 0.036 gm.

Weight of carbon dioxide = 0.220 gm.

$$\begin{aligned} \therefore \text{Percentage of carbon} &= \frac{12}{44} \times 0.22 \times \frac{100}{0.24} \\ &= 25.00 \end{aligned}$$

$$\begin{aligned} \text{Percentage of hydrogen} &= \frac{2}{18} \times 0.036 \times \frac{100}{0.24} \\ &= 1.66 \end{aligned}$$

$$\begin{aligned} \therefore \text{Percentage of oxygen (by difference)} &= 100 - 25.00 - 1.66 = 73.34 \end{aligned}$$

Thus the percentage composition of the compound is:

$$\text{C} = 25.00$$

$$\text{H} = 1.66$$

$$\text{O} = 73.34$$

Estimation of Nitrogen. Nitrogen is estimated by two methods. The first is known as **Dumas method** and is applicable in the case of all organic substances. The second method is known as **Kjeldahl's method**. This is of limited application as it cannot be used in the case of those compounds which contain nitrogen atoms linked either to oxygen or to other nitrogen atoms. Both the methods are described below :

Dumas' Method. The method consists in heating the organic compound with cupric oxide in an atmosphere of carbon dioxide. The carbon and hydrogen are oxidised to carbon dioxide and water (steam) respectively. Sulphur, if present, is oxidised to sulphur dioxide while nitrogen is set free. If any oxide of nitrogen is produced, it is reduced back to nitrogen by passing over hot shining copper gauze. The gases are then led into a special apparatus known as Schiff's nitrometer (Fig. 3) which is filled with 30 per cent potassium hydroxide solution. Carbon dioxide and sulphur dioxide are absorbed by KOH, steam condenses, while nitrogen collects over potash in the nitrometer. Its volume is noted.

Apparatus. The apparatus is shown in Fig. 3. It consists of :

(i) *A carbon dioxide generator* which is usually a hard glass tube containing sodium bicarbonate.

(ii) *A combustion tube* which is essentially a hard glass or pyrex glass tube open at both ends and about 10 cm. longer than the combustion furnace in which it is placed.

The combustion tube is filled as shown in the figure.

(iii) *A Schiff's nitrometer* which is simply a gas burette filled with 30 per cent potassium hydroxide solution and a little mercury as shown. The mercury serves the function of a valve as it lets the gases to pass into the nitrometer but prevents the back flow of the potash solution.

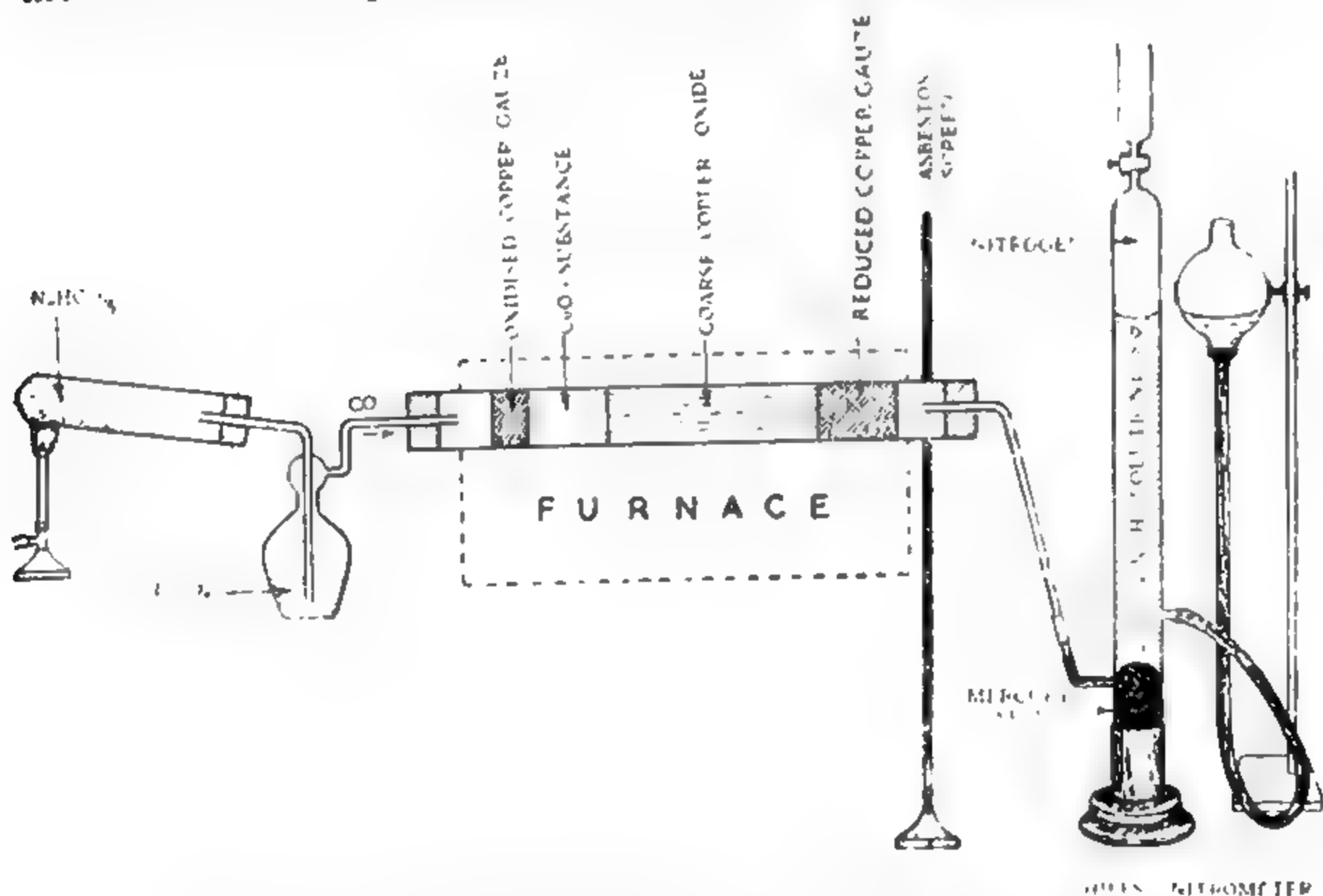


Fig. 3. Apparatus for the estimation of nitrogen by Dumas' method.

Procedure. A weighed amount of the substance under examination is thoroughly mixed with fine cupric oxide and is introduced into the combustion tube in the position indicated in the figure. The weight of the substance should be such as to give between 30 to 40 ml. of free nitrogen.

The bright reduced copper gauze placed at the end of the tube on the nitrometer side helps to reduce any oxides of nitrogen that may be formed.

The oxidised copper gauze placed at the beginning of the tube serves to oxidise any vapour of the substance which might diffuse back wards. It is *essential first of all to displace all air from the combustion tube*. For this purpose, the carbon dioxide produced by gently heating the sodium bicarbonate is made to sweep through the tube. After some time when it is thought that the air has been completely displaced, the reservoir of the nitrometer is raised so as to fill it completely with potassium hydroxide solution. The tap is then closed. If the air has been completely displaced, subsequent passage of carbon dioxide will not cause any fall in the level of potassium hydroxide solution in the nitrometer.

The combustion tube is then heated in the furnace, first at the two ends and then gently in the middle where the mixture of the organic substance with the copper oxide is located. The gentle and continuous heating of the mixture results in the bubbling of nitrogen slowly and steadily into the nitrometer. A slow stream of carbon dioxide is maintained throughout to avoid back flow of the gases. When further evolution of nitrogen slows down, the current of carbon dioxide is increased so as to sweep away all residual or sticking nitrogen into the nitrometer.

When no more nitrogen collects in the nitrometer, it is disconnected and cooled for an hour or so to bring it at the room temperature. The volume of nitrogen is then noted after bringing the level of the potash solution in the two limbs at the same height. *The temperature and barometric pressure are noted at the same time*. It is also necessary to know the *aqueous tension* (or more accurately the vapour pressure of water over 30 per cent solution of potassium hydroxide) at the prevailing temperature.

The percentage of nitrogen is then determined as below :

Calculations.

Suppose weight of the substance = w gm.

Volume of nitrogen collected = V_1 c.c.

Barometric pressure = P mm. of Hg

Aqueous tension = p mm. of Hg

Room temperature = $t^\circ \text{C}$

Then volume (V) of nitrogen at N.T.P. is given by

$$\frac{(P-p)V_1}{(273+t)} = \frac{760 \times V}{273}$$

$$\text{or } V = \frac{(P-p) V_1 \times 273}{(273+t) \times 760} = x \text{ c.c. (say)}$$

Since 22,400 c.c. of nitrogen at N.T.P. weigh equal to its gram-molecular weight, viz., 28 gm.,

$$\therefore \text{Weight of } x \text{ c.c. of nitrogen at N.T.P.} = \frac{28 \times x}{22400} \text{ gm.}$$

$$\therefore \text{Percentage of nitrogen} = \frac{28 \times x \times 100}{22400 \times w}$$

Example 3. 0.200 gm. of an organic compound gave on combustion 40.5 ml. of dry nitrogen at 27°C and 740 mm. pressure. Find the percentage of nitrogen in the compound.

Weight of substance = 0.200 gm.

$V = 40.5$ ml.

$P = 740$ mm.

$T = 273 + 27 = 300^\circ\text{A}$

$V_1 = ?$

$P_1 = 760$ mm.

$T_1 = 273$ A

$$\frac{V_1 P_1}{T_1} = \frac{VP}{T}$$

$$\therefore V_1, \text{ the volume of nitrogen at N.T.P.} = \frac{40.5 \times 740 \times 273}{760 \times 300} = 35.89 \text{ ml.}$$

$$\text{Weight of nitrogen in 0.200 gm. of the substance} = \frac{28 \times 35.89}{22,400} \text{ gm.}$$

$$\therefore \text{Percentage of nitrogen} = \frac{28 \times 35.89 \times 100}{22400 \times 0.200} = 22.5\%$$

Example 4. 0.423 gm. of an organic compound gave on combustion 43.2 ml. of nitrogen measured at 19.5°C and 733.5 mm. pressure. Find the percentage of nitrogen in the compound. Aqueous tension at 19.5° is 17.8 mm.

Weight of the substance = 0.423 gm.

$V = 43.2$ ml.

$P = 733.5 - 17.8 = 715.7$ mm.

$T = 292.5^\circ\text{A}$

$V_1 = ?$

$P_1 = 760$ mm.

$T_1 = 273$ A

$$\frac{V_1 P_1}{T_1} = \frac{VP}{T}$$

$$V_1, \text{ the volume of nitrogen at N.T.P.} = \frac{43.2 \times 715.7 \times 273}{292.5 \times 760} = 37.97 \text{ ml.}$$

$$\therefore \text{Percentage of nitrogen} = \frac{28 \times 37.97 \times 100}{22,400 \times 0.423} = 11.22\%$$

Kjeldahl's Method. This method is based upon the fact that many nitrogenous organic substances when heated strongly in concentrated sulphuric acid are converted quantitatively into ammonium sulphate. The ammonium sulphate solution so obtained is heated with excess of sodium hydroxide. The ammonia gas thus liberated is absorbed in a known volume (excess) of a standard solution of hydrochloric acid or sulphuric acid. The decrease in the concentration of the acid (as obtained by titrating against a standard alkali) corresponds to the amount of ammonia liberated from the organic compound from which the percentage of nitrogen in the compound can be calculated.

The reactions involved are :



The ammonia gas is absorbed in excess of sulphuric acid forming ammonium sulphate.



The sulphuric acid left behind is titrated back with a standard solution of sodium hydroxide. From the amount of sulphuric acid used up in reaction (iii), the amount of ammonia and hence that of nitrogen in the original compound can be calculated.

Procedure. The process consists of three steps :

(1) *Conversion to ammonium sulphate.* A weighed amount of the substance (usually 0.2 to 0.4 gm.) is mixed with about 30 ml. of concentrated

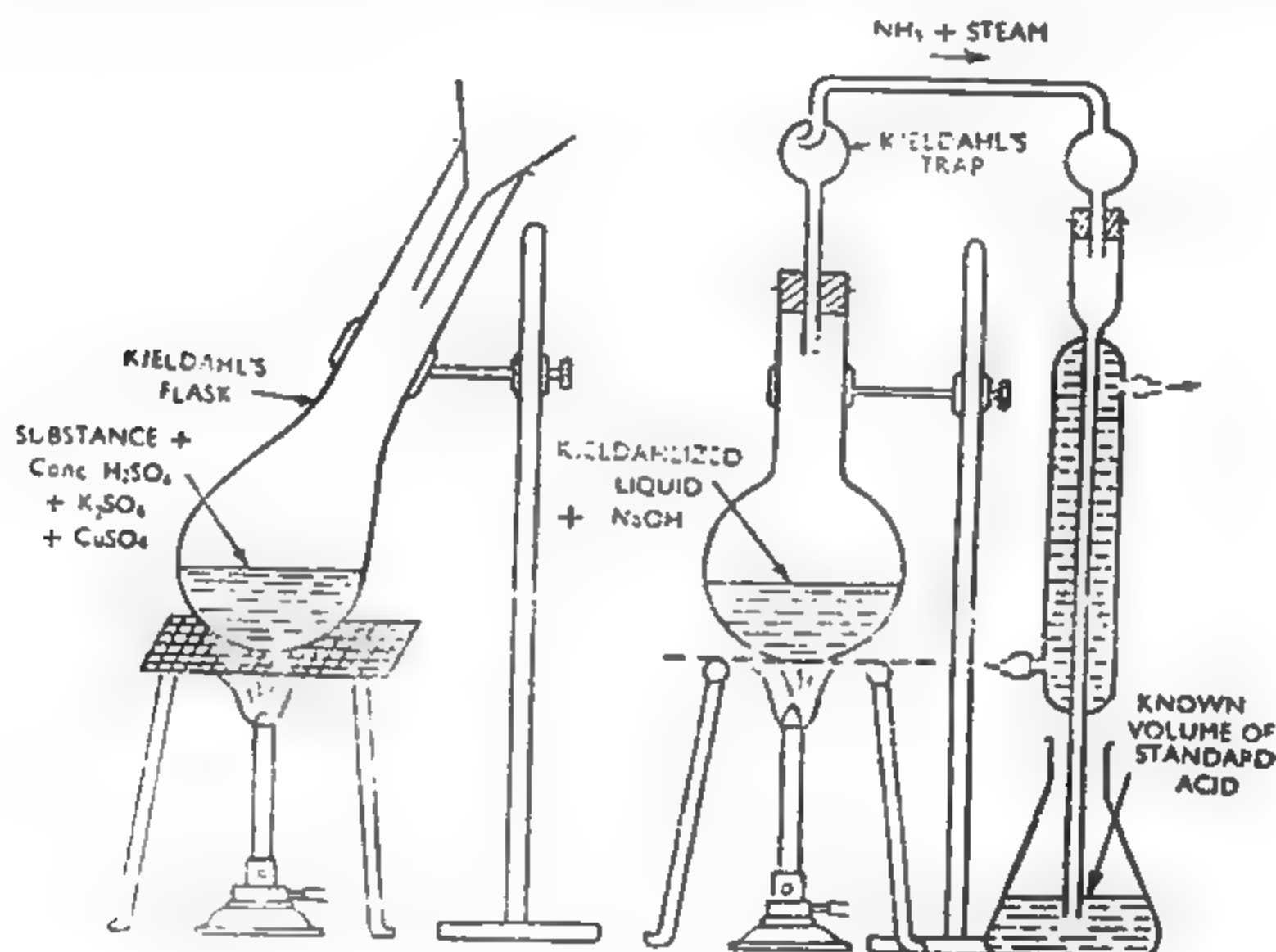


Fig. 4. Estimation of Nitrogen by Kjeldahl's Method.

sulphuric acid in a long-necked round-bottomed flask known as Kjeldahl's flask (Fig. 4). The mixture is heated in a fumes-cupboard for about 30 minutes after which a small amount of potassium sulphate is added to raise the boiling point of the acid. A few crystals of copper sulphate or a few drops of mercury are generally added which are known to catalyse the reaction. The mixture is boiled for two to three hours *until a clear solution results*. This indicates that the nitrogen has completely changed into ammonium sulphate.

(2) *Distillation with alkali.* The contents of the Kjeldahl's flask are cooled and poured into about 100 ml. of water containing a drop of

two of methyl orange placed in 500 ml. round-bottomed flask. The flask is provided with a thistle funnel and is also connected through a trap (*Kjeldahl's trap*) to a vertical condenser which ends in a conical flask containing a measured excess of a standard acid (Fig 4).

A 30 per cent solution of sodium hydroxide is run into the flask through the thistle funnel until the mixture is just alkaline as indicated by change in colour of methyl orange. The mixture is then heated to boiling after adding an excess of sodium hydroxide. Ammonia gas begins to be evolved gradually along with steam. This passes through the condenser into the standard solution of the acid.

(3) *Estimation of ammonia.* After some time, the evolution of ammonia ceases. The conical flask is then dismantled and the acid is made up to 250 ml volume. Portions of this acid are titrated against standard sodium hydroxide solution using methyl orange as the indicator.

The Kjeldahl's trap prevents the passage of any solution from the distillation flask into the conical flask due to bumping, if any.

Calculations. Suppose w gm. of the substance is taken and that V_1 ml. of acid of normality N_1 is required for the neutralisation of ammonia evolved.

Now V_1 ml. of acid of normality $N_1 \equiv V_1$ ml. of NH_3 of normality N_1

But 1000 ml. of normal ammonia $\equiv 17$ gm. of NH_3
 $\equiv 14$ gm. of nitrogen

$\therefore V_1$ ml. of ammonia of normality N_1

$\equiv \frac{14}{1000} \times V_1 \times N_1$ gm. of nitrogen

\therefore Percentage of nitrogen $= \frac{14 \times V_1 \times N_1}{1000} \times \frac{100}{w}$

$= \frac{1.4 N_1 V_1}{w}$

Example 5. 0.420 gm. of an organic substance was kjeldahlised. The ammonia, evolved on distilling with excess of NaOH , neutralised 37.50 ml. of $N/10 \text{ H}_2\text{SO}_4$. What is the percentage of nitrogen in the compound?

Weight of the substance = 0.420 gm.

Volume of $N/10 \text{ H}_2\text{SO}_4$ required for the neutralization of ammonia = 37.50 ml.
 $\equiv 37.50$ ml. of $N/10 \text{ NH}_3$
 $\equiv 17$ gm. of NH_3
 $\equiv 14$ gm. of nitrogen

\therefore Percentage of nitrogen $= \frac{14 \times 37.5}{1000} \times \frac{1}{10} \times \frac{100}{0.42}$
 $= 12.4$

Example 6. 0.2340 gm. of an organic substance containing nitrogen was kjeldahlised and the ammonia evolved was absorbed in 90.35 ml. of 0.1 N hydrochloric acid. The excess of the acid required 20.0 ml. of $N/5 \text{ NaOH}$ for neutralization. Calculate the percentage of nitrogen.

Weight of the substance = 0.2340 gm.

Volume of 0.1N HCl taken = 90.35 ml.

Let the volume of the acid left

unused = x ml.

$\therefore x$ ml. of 0.1 N HCl \equiv 20.0 ml. of $N/5$ NaOH

$\therefore x = 40$ ml.

\therefore Volume of the acid used

in neutralizing the ammonia = (90.35—40) ml.

= 50.35 ml.

50.35 ml. of 0.1 N HCl \equiv 50.35 ml. of 0.1N NH_3

But 1000 ml. of N . NH_3 \equiv 17 gm. of ammonia

\equiv 14 gm. of nitrogen

\therefore Percentage of nitrogen $\equiv \frac{14 \times 50.35 \times 0.1 \times 100}{1000 \times 0.234}$

= 30.12

Example 7. 0.45 gm. of a substance was kjeldahlised and the ammonia obtained was passed into 60 ml. of decinormal sulphuric acid. The excess of the acid was diluted and the volume made up to 250 ml. 25 ml. of this solution required 10 ml. of $N/40$ NaOH for neutralization. Calculate the percentage of nitrogen in the compound.

Weight of the substance = 0.45 gm.

Vol. of $N/10$ sulphuric acid taken = 60 ml.

Let the vol. of $N/10$ sulphuric acid

left unused = x ml.

This volume (x ml.) has been diluted to 250 ml.

25 ml. of the diluted solution \equiv 10 ml. of $N/40$ NaOH

\therefore 250 ml. of the diluted solution $\equiv 10 \times \frac{250}{25}$ ml. of $\frac{N}{40}$ NaOH

\equiv 100 ml. of $\frac{N}{40}$ NaOH

But 250 ml. of the diluted solution $\equiv x$ ml. of $N/10$ H_2SO_4

$\therefore x$ ml. of $N/10$ H_2SO_4 \equiv 100 ml. of $N/40$ NaOH

$x = 25$ ml.

\therefore The volume of the $N/10$ acid

used for neutralizing ammonia = 60—25 = 35 ml.

35 ml. of $N/10$ acid \equiv 35 ml. of $N/10$ NH_3

But 1000 ml. of N . NH_3 \equiv 17 gm. of NH_3

\equiv 14 gm. of nitrogen

\therefore Percentage of nitrogen = $\frac{14 \times 1 \times 35 \times 100}{1000 \times 10 \times 0.45}$

= 10.89

Estimation of Halogens. Carius Method. It consists in heating a known weight of the substance with fuming nitric acid in the presence of silver nitrate at $260-270^\circ$ for about 6 hours in a special tube known as **Carius tube**. The Carius tube is made up of special hard glass and is 20 cm. in length and 2 cm. in diameter (Fig. 5.). The carbon and hydrogen are oxidised to carbon dioxide and water while the halogen, if present, reacts with silver nitrate giving a precipitate of silver halide. This is separated, washed, dried and weighed.

Procedure. About 0.5 gm. of silver nitrate and 5 ml. of fuming nitric acid are added to the tube. A weighed amount (about 0.2 gm.) of the substance, taken in a small test tube, is introduced carefully along the side into the Carius tube which is then drawn out and sealed. The open end of the test tube stands above the fuming nitric acid as shown. The Carius tube is then wrapped in an asbestos paper and heated in a "bomb furnace" at $260-270^\circ\text{C}$ for about 4-6 hours. The furnace is then put off and the tube is allowed to cool gradually. The sealed capillary end is then heated as a result of which the glass softens and a small hole opens out through which the compressed gases within the tube come out slowly. Finally the capillary end is cut off and the contents transferred into a beaker. The silver halide formed is separated by filtration over a Gooch crucible, washed, dried and weighed.

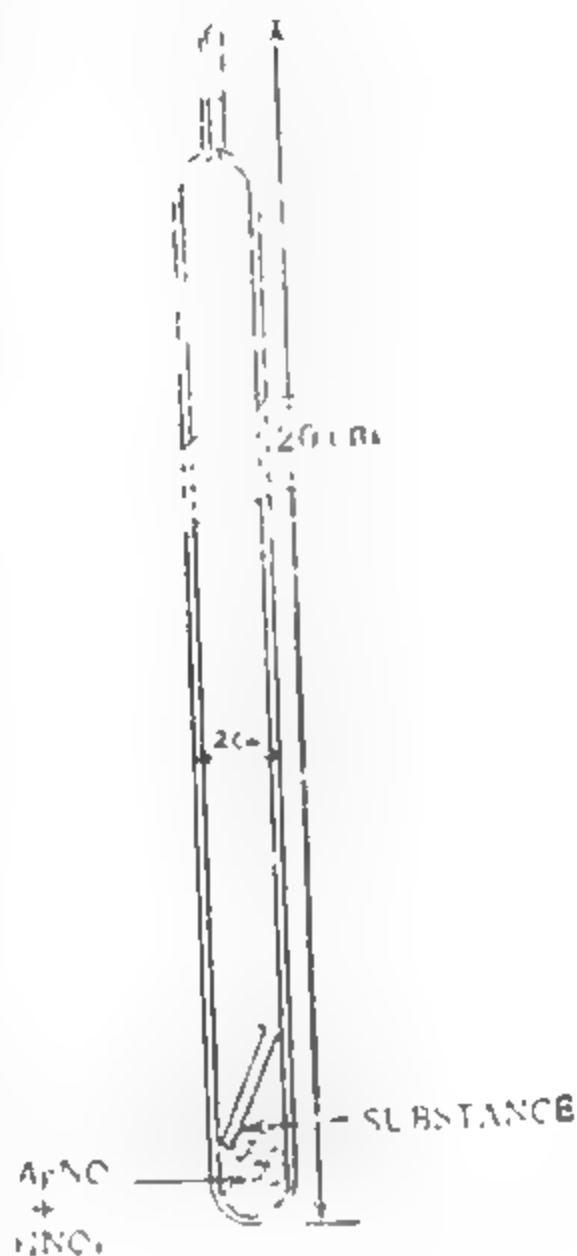


Fig. 5. The Carius tube

Calculations

Suppose wt. of the substance taken = w gm.

Wt. of the silver halide (AgX) formed = x gm.

Now, molecular weight of AgX \equiv Atomic wt. of X

\therefore Wt. of the halogen in w gm. of the substance

$$= \frac{\text{At. wt. of X}}{\text{Mol. wt. of AgX}} \times x$$

$$= \frac{\text{At. wt. of X} \times x \times 100}{\text{Mol. wt. of AgX} \times w}$$

\therefore Percentage of the halogen

For example,

If the halogen present is chlorine, the silver halide formed will be AgCl

1 molecule of $\text{AgCl} \equiv$ 1 atom of chlorine

or $108 + 35.5 = 143.5$ gm. of $\text{AgCl} \equiv 35.5$ gm. of chlorine

$$\therefore \text{Percentage of chlorine} = \frac{35.5 \times x \times 100}{143.5 \times w}$$

where x is the weight of AgCl formed from w gm. of the substance.

Similarly, the *percentage of bromine* will be given by the expression

$$\frac{80 \times x' \times 100}{188 \times w}$$

where x' is the weight of AgBr formed.

It is important to note that the Carius method does not give good results in the case of iodine.

Example 8. 0.185 gm. of an organic substance when treated in Carius tube gave 0.320 gm. of silver bromide. Calculate the percentage of bromine in the compound.

	Wt. of the substance	= 0.185 gm.
	Wt. of silver bromide	= 0.320 gm.
	1 molecule of AgBr	\equiv 1 atom of Br
or	188 gm. of AgBr	\equiv 80 gm. of Br
\therefore	0.320 gm. of AgBr	$\equiv \frac{80}{188} \times 0.320$ gm. of Br
\therefore	Percentage of bromine	$= \frac{80}{188} \times 0.320 \times \frac{100}{0.185}$ $= 73.60$

Example 9. 0.1890 gm. of an organic substance on heating with fuming nitric acid and silver nitrate in Carius tube produced 0.287 gm. of silver chloride. What is the percentage of chlorine in the compound?

	Wt. of the substance	= 0.1890 gm.
	Wt. of the silver chloride	= 0.287 gm.
	143.5 of AgCl	\equiv 35.5 gm. of chlorine
\therefore	0.287 gm. of AgCl	$\equiv \frac{35.5}{143.5} \times 0.287$ gm. of Cl
\therefore	Percentage of chlorine	$= \frac{35.5}{143.5} \times 0.287 \times \frac{100}{0.189}$ $= 37.58$

Estimation of Sulphur. Sulphur is also estimated by Carius method. But silver nitrate is used in this case. The sulphur present in the substance is oxidised by fuming nitric acid into sulphuric acid which is then completely precipitated as barium sulphate on the addition of excess of barium chloride. The precipitate is filtered, washed, dried and weighed.

Calculations. Suppose w gm. of the organic substance yields x gm. of BaSO_4 .

Molecular weight of BaSO_4	= 233
Now, 233 gm. of BaSO_4	\equiv 32 gm. of S

ESTIMATION OF PHOSPHORUS

$$\begin{aligned} \therefore x \text{ gm. of BaSO}_4 & \equiv \frac{32 \times x}{233} \text{ gm. of S} \\ \therefore \text{Percentage of sulphur} & = \frac{32 \times x}{233} \times \frac{100}{w} \end{aligned}$$

Example 10. 0.2650 gm. of an organic substance gave 0.450 gm. of barium sulphate in a Carius determination. Calculate the percentage of sulphur.

$$\begin{aligned} \text{Wt. of the substance} & = 0.265 \text{ gm.} \\ \text{Wt. of BaSO}_4 & = 0.450 \text{ gm.} \\ 233 \text{ gm. of BaSO}_4 & \equiv 32 \text{ gm. of S} \\ \therefore \text{Percentage of sulphur} & = \frac{32}{233} \times 0.45 \times \frac{100}{0.265} \\ & = 23.32 \end{aligned}$$

Estimation of Phosphorus. Phosphorus may also be estimated by the Carius method. But the results are not satisfactory since phosphorus is not completely oxidised to phosphoric acid by fuming nitric acid. Best results are obtained by heating the compound with fusion mixture. The phosphate obtained is treated with magnesia mixture when crystalline precipitate of MgNH_4PO_4 is obtained. It is ignited to yield $\text{Mg}_2\text{P}_2\text{O}_7$. From the weight of $\text{Mg}_2\text{P}_2\text{O}_7$ (magnesium pyrophosphate) the percentage of phosphorus can be calculated as below :

$$\begin{aligned} \text{Let the wt. of substance} & = w \text{ gm.} \\ \text{Wt. of Mg}_2\text{P}_2\text{O}_7 & = x \text{ gm.} \\ \text{Molecular weight of Mg}_2\text{P}_2\text{O}_7 & = 222 \\ \text{Now 222 gm. of Mg}_2\text{P}_2\text{O}_7 & \equiv 62 \text{ gm. of P} \\ \therefore \text{Percentage of phosphorus} & = \frac{62 \times x \times 100}{222 \times w} \end{aligned}$$

Example 11. 0.30 gm. of an organic substance containing phosphorus gave 0.55 gm. of $\text{Mg}_2\text{P}_2\text{O}_7$ by usual analysis. Calculate the percentage of phosphorus in the compound.

$$\begin{aligned} \text{Wt. of the substance} & = 0.30 \text{ gm.} \\ \text{Wt. of Mg}_2\text{P}_2\text{O}_7 & = 0.550 \text{ gm.} \\ 222 \text{ gm. of Mg}_2\text{P}_2\text{O}_7 & = 62 \text{ gm. of P} \\ \therefore \text{Percentage of phosphorus} & = \frac{62 \times 0.55 \times 100}{222 \times 0.30} \\ & = 51.20 \end{aligned}$$

Estimation of oxygen. The quantitative estimation of oxygen is rather difficult. The percentage of oxygen is usually obtained by method of difference.

However, recently a satisfactory method for the estimation of oxygen has been worked out. It consists of heating strongly the oxygen bearing compound in a stream of nitrogen and passing the gases evolved over excess of hot carbon. The oxygen is converted into carbon monoxide. It is passed over iodine pent-oxide to liberate iodine which is estimated volumetrically by titrating against standard sodium thiosulphate solution.



QUESTIONS

1. Describe with the help of a diagram, the method for estimating carbon and hydrogen in a compound which contains neither chlorine nor sulphur.

What precautions would you take if the compound, besides carbon and hydrogen, contains any one of the following elements : (i) Sulphur (ii) Nitrogen (iii) Halogens.

2. Describe the method for estimating carbon and hydrogen in an organic compound. Give in details the function of the various parts of the apparatus used.

3. Describe Dumas' method for the estimation of nitrogen in an organic compound. Mention clearly the function of each part of the apparatus.

4. Give in details the Kjeldahl's method for the estimation of nitrogen in an organic compound. In what type of compounds the method fails? What procedure is adopted to avoid 'bumping' of the solution during heating.

5. Describe the Carius method for the estimation of halogens in an organic compound. What modification is required if sulphur is to be estimated by Carius method?

6. Explain clearly but concisely how sulphur and phosphorus may be estimated in an organic compound.

7. Describe with the help of a diagram the method of estimating carbon and hydrogen in an organic compound, indicating clearly the method of filling the tube.

(*Panjab Inter. 1945, 1962*)

8 (a) Describe briefly but precisely a method for the estimation of carbon and hydrogen in organic compounds, containing neither sulphur nor chlorine.

(b) 0.2475 gm. of an organic substance gave on combustion 0.9450 gm. of CO_2 and 0.2025 gm. of H_2O . Calculate the percentage of carbon and hydrogen.

(Ans. $\text{C}=54.44\%$; $\text{H}=9.09\%$) (*Panjab Inter. 1959*)

9. Describe the Dumas' method for the estimation of nitrogen. Draw the sketch of the apparatus and explain the action of its parts.

(*Panjab Inter. 1949, 1956*)

10. 0.2046 gm. of an organic substance gave 30.4 c.c. of moist nitrogen measured at 15°C and 732.7 m.m. pressure. Calculate the percentage of nitrogen in the compound. Aqueous tension at 15°C is 12.7 m.m. and one litre of nitrogen weighs 1.25 gm. at N.T.P.

(Ans. 16.67%) (*Panjab Inter. 1943*)

11. An organic compound gave following results on analysis :

0.1335 gm. gave 0.2948 gm. of CO_2 and 0.0603 gm. H_2O . 0.085 gm. gave 26.4 c.c. of dry nitrogen measured at 27°C and 750 m.m. pressure. Calculate the percentage composition of the compound.

(Ans. $\text{C}=60.22\%$; $\text{H}=5.02\%$; $\text{N}=34.85\%$) (*Panjab Inter. 1949*)

12. 0.27 gm. of an organic compound gave on combustion 0.396 gm. of CO_2 and 0.216 gm. of H_2O . 0.36 gm. of the substance gave 48.88 c.c. of dry nitrogen at 26°C and 740 m.m. pressure. Calculate the percentage of carbon, hydrogen and nitrogen.

(Ans. $\text{C}=40\%$; $\text{H}=8.89\%$; $\text{N}=15.55\%$) (*Panjab Inter. 1958*)

13. Describe Kjeldahl's method for the estimation of nitrogen in an organic compound.

(*Panjab Inter. 1950, 1952, 1956, 1959 S, 1960*)

14. 0.1560 gm. of a nitrogenous substance was Kjeldahlised and the ammonia gas evolved from it was absorbed in 60.25 ml. of $\text{N}/10 \text{H}_2\text{SO}_4$. After absorption the excess of the acid required 26.50 ml. of $\text{N}/10 \text{NaOH}$ for exact neutralization. Calculate the percentage of nitrogen in the compound.

(Ans. 39.26%) (*Panjab Inter. 1950*)

15. Ammonia produced when 0.75 gm. of a substance was Kjeldahlised neutralized 30 ml. of $0.25 \text{N} \text{H}_2\text{SO}_4$. Calculate the percentage of nitrogen in the compound.

(Ans. 14.00%) (*Panjab Inter. 1959*)

16. 0.789 gm. of an organic substance after being digested with sulphuric acid was distilled with excess of caustic soda. The liberated ammonia was absorbed in 100 ml. of $\text{N} \text{H}_2\text{SO}_4$. The excess acid left after absorption required 73.7 ml. of $\text{N} \text{NaOH}$ for neutralization. Calculate the percentage of nitrogen.

(Ans. 46.60%) (*Panjab Inter. 1960*)

17. With the help of a diagram, explain the method of estimation of bromine in an organic compound.

0.301 gm. of an organic compound gave 0.282 gm. of silver bromide in a halogen estimation method. Find the percentage of bromine in the compound
(Ans. 39.86%) (Panjab Inter 1958)

18. Give in details (including calculations) Carius method of estimation of halogens in an organic compound.
(Panjab Inter 1961)

0.16 gm. of an organic compound containing sulphur gave after suitable treatment 0.1167 gm. of barium sulphate. Calculate the percentage of sulphur in the compound.
(Ans. 10.01%) (Panjab Inter 1961)

19. Outline one method for the determination of carbon and hydrogen in organic compounds. Explain the principle used.
(Panjab Pre Med., 1957)

20. How is nitrogen detected in an organic compound? Explain as far as possible the reactions involved by means of equations.

0.257 gm. of an organic substance was Kjeldahlised and ammonia evolved was absorbed in 50 ml. of N/10 HCl which required 23.2 ml. of N/10 NaOH for neutralisation. Determine the percentage of nitrogen in the substance. (Panjab Inter. 1962)

21. Fill in the blanks

(i) The function of bright copper spiral in Dumas' method is to convert to

(ii) Kjeldahl method fails when.....is present as.....

(iii) Carius method is used for estimation of.....and.....

(iv) The function of potash bulbs and calcium chloride U-tube in Liebig's method areand.....respectively.

(i) In Liebig's method for estimation of carbon and hydrogen free air is used (why?)

22. (a) Explain with the help of a diagram the estimation of carbon and hydrogen in an organic compound.

(b) 1.2 gm. of organic substance gave 21.8 ml of nitrogen at 15°C and 760 mm. pressure. Calculate the percentage of the substance.
(Ans. 12.9) (Panjab T.D.C Part I 1964 S)

23. (a) Outline the estimation of sulphur by Carius method.

(b) 0.32 gm. of an organic compound containing sulphur yielded 0.2334 gm. of barium sulphate. Calculate the percentage of sulphur in the compound. (Ans 10.01%)
(Panjab T.D.C (I) 1966)

24. Describe briefly, with the help of a labelled diagram, the estimation of carbon and hydrogen in an organic compound containing also nitrogen, sulphur and chlorine. Give chemical reactions involved
(Panjab Pre Eng. Med 1966)

25. (a) Draw an indicative diagram to show the estimation of Nitrogen by Dumas' method. Briefly explain the principle underlying this method.

(b) 1.5 gm., of an organic substance was combusted in a hard glass combustion tube for estimation of nitrogen by Dumas, method. The volume of dry nitrogen collected at 27°C and 700 mm, pressure was found to be 300 ml. Calculate the percentage of nitrogen in the substance.
(Panjab T.D.C. Part I 1963 S)

CHAPTER XXI

DETERMINATION OF MOLECULAR WEIGHTS

Molecular Weight. Molecular weight of a substance is defined as *weight of one molecule of the substance as compared to that of the weight of oxygen atom taken as 16*. A number of methods for determining molecular weights of organic compounds are known. They generally fall into two groups.

(A) *Physical methods* and (B) *Chemical methods*.

A. Physical Methods.

(i) *For Volatile Substances. Victor Meyer's Method.* This is the most convenient method for determining molecular weights of volatile substances.

The method consists in volatilising a known weight of the substance by dropping it in a heated glass tube. The vapour displaces an equal volume of air which is collected by the downward displacement of water.

Apparatus. It consists of

(i) An outer jacket 'J' usually made of copper in which is placed a liquid whose boiling point is $20-30^{\circ}$ higher than that of the volatile substance under examination.

(ii) An inner glass tube, *A*, called Victor Meyer's tube having a long bulb below, a side tube *S* and a funnel shaped opening *F* at the top, which can be corked.

(iii) A graduated gas burette for collecting the displaced air over water.

(iv) A very small stoppered bottle known as Hofmann's bottle (*H*), in which a small weighed amount of the volatile substance is placed.

Procedure The liquid (usually water) in the outer jacket *J* is heated to boiling. In the meantime, the Victor Meyer's tube is thoroughly cleaned and dried. A small amount of glass wool or asbestos is placed at its bottom. It is then tightly corked and introduced into the outer jacket as shown in Fig. 1. The air inside the tube expands, and comes out of the side tube. After 15–20 minutes when practically the whole of the expanded air has been driven out of the Victor Meyer's tube *A*, the side tube *S* is connected to the gas burette. The level of water is

raised to the top of the burette with the help of the reservoir *R*. When no more of air comes into the burette from the tube *A*, the water level shows a constant reading. The level of water in the two limbs is brought at the same height and the reading recorded.

A small amount, usually 0.1 to 0.2 gm. of the volatile substance, which is sufficient to give about 30 to 40 c.c. of vapour is accurately weighed in the Hofmann's bottle. This loosely stoppered bottle is immediately dropped into Victor Meyer's tube by removing its cork momentarily. The presence of the glass wool pad prevents its breakage.

The substance readily changes into the vapour and the stopper of the Hofmann's bottle is blown out. The displaced air collects in the graduated gas burette by the downward displacement of water. When there is no further fall in the level of water, the burette is closed with the help of the

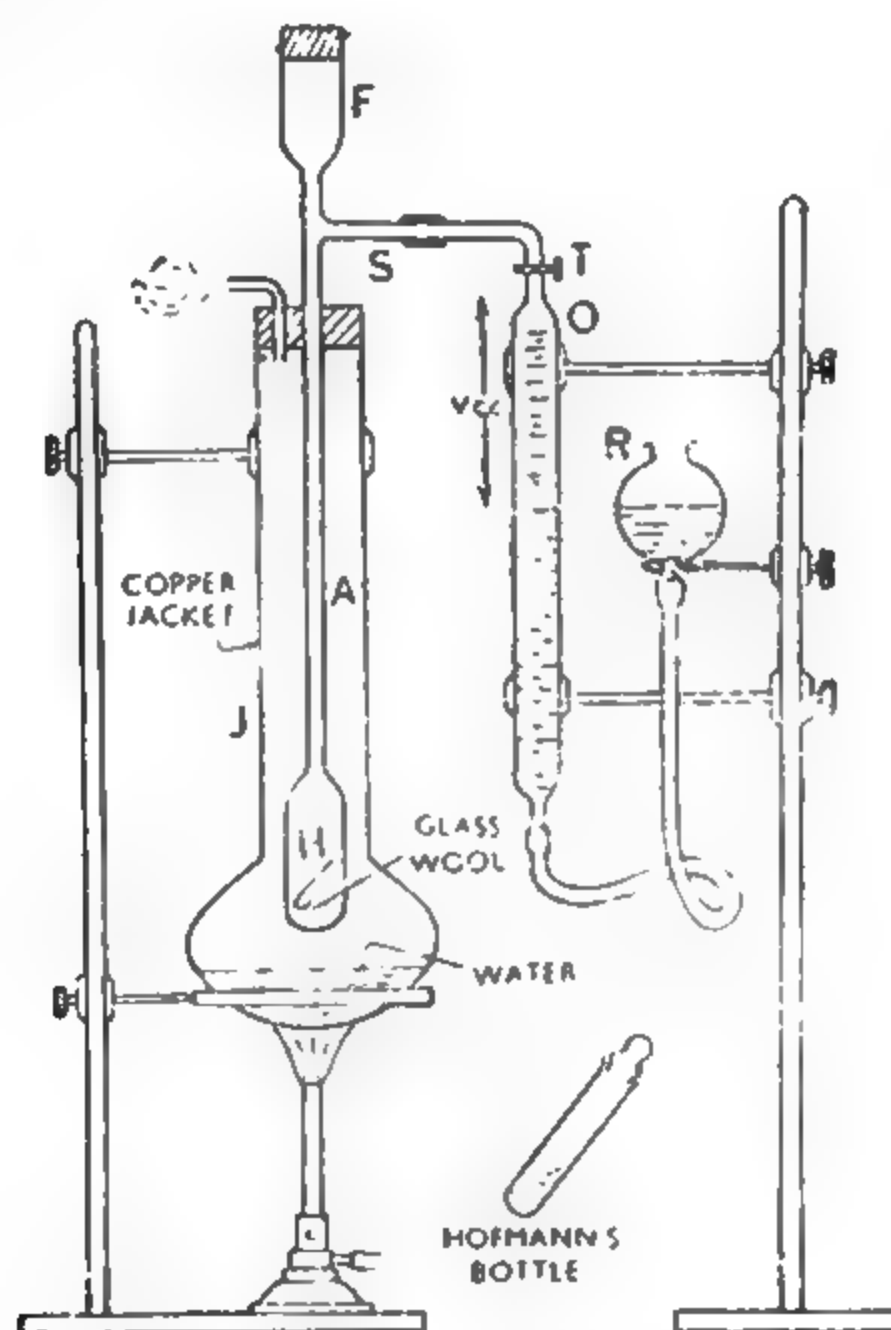


Fig. 6.1. Victor Meyer's apparatus

stop cock *T*. The volume of air collected is noted after making the water level same in both the limbs. The room temperature and barometric pressure are also noted.

Calculations. Suppose *w* gm. of the volatile liquid displace *V* c.c. of moist air at pressure *P* and temperature *T*° (absolute).

The volume (V_1) of air at *N.T.P.* is given by

$$\frac{760 \times V_1}{273} = \frac{(P-p)V}{T}$$

where p is aqueous tension at temperature T .

Thus, V_1 c.c. of the vapour at *N.T.P.* weigh w gm. Since 22,400 c.c. of every gas or vapour at *N.T.P.* weigh equal to the molecular weight of the gas or vapour.

$$\therefore \text{Molecular weight of the substance} = \frac{w \times 22400}{V_1}$$

Example. 1. 0.150 gm. of a volatile liquid displaced 40.5 ml. of air collected over water at 15°C and 746 mm. pressure. Calculate the molecular weight of the liquid. (Aqueous tension at 15°C may be taken as 13.7 mm).

$$\text{Weight of the substance} = 0.150 \text{ gm.}$$

$$V = 40.5 \text{ ml.} \quad V_1 = ?$$

$$P = 746 - 13.7 = 732.3 \text{ mm.} \quad P_1 = 760 \text{ mm.}$$

$$T = 15 + 273 = 288^\circ\text{A} \quad T_1 = 273^\circ\text{A}$$

$$\frac{V_1 P_1}{T_1} = \frac{VP}{T}$$

$$V_1, \text{ the volume of air at } N.T.P. = \frac{40.5 \times 732.3 \times 273}{288 \times 760}$$

$$= 37.07 \text{ ml.}$$

$$\therefore \text{Molecular weight of the substance} = \frac{0.150 \times 22400}{37.07}$$

$$= 90.68$$

(ii) *For Non-volatile Substances.* If the organic substance is nonvolatile, the molecular weight is determined by measuring either (a) *Depression in freezing point* (b) *Elevation in boiling point* of a solvent caused by dissolving a known (small) weight of the solute in a known weight of the solvent.

It is a well-known fact of physical chemistry that when one gram mole (molecular weight in grams) of any substance is dissolved in a fixed amount of the solvent, the freezing point of the liquid is lowered (and the boiling point is raised) to a certain extent. For instance, it is known that when 1 gm. mole of any organic solute is dissolved in 100 gm. of water, the freezing point is always lowered by 1.86° and boiling point is raised by 5.2° . These values are known as molecular depression constant and molecular elevation constant of water respectively. Similarly, molecular depression constant of benzene is 51.2° and molecular elevation constant is 287° .

Calculation of molecular weight. Suppose w gm. of a non-volatile solute when dissolved in W gm. of a solvent cause a lowering of freezing point equal to ΔT . Let K_f be the molecular depression constant of the solvent. If m is the molecular weight of the solute, then by definition :

m gm. of the solute dissolved in 100 gm. of the solvent will cause a depression of K_f ... (1)

Also, according to the question, w gm. of the solute dissolved in W gm. of the solvent cause a depression of ΔT° .

or $\frac{w}{W} \times 100$ gm. of the solute dissolved in 100 gm. of the solvent will cause a depression of ΔT° (2)

From (1) and (2)

$$\frac{m}{\frac{w}{W} \times 100} = \frac{K_f}{\Delta T}$$

or

$$m = \frac{100 K_f w}{W \Delta T}$$

With the help of this equation, the molecular weight of a non-volatile solute can be easily determined.

Example 2. 1.26 gm. of a solute was dissolved in 93 gm. of water when the solution was found to freeze at -0.42°C . Calculate the molecular weight of the solute. (K_f for water is 18.6° per 100 gm.).

$$\begin{aligned} m &= \frac{100 K_f w}{W \Delta T} \\ &= \frac{100 \times 18.6 \times 1.26}{93 \times 0.42} = 60.0 \end{aligned}$$

Example 3. 2.5 gm. of an organic substance when dissolved in 75 gm of acetone raised the boiling point by 0.43°C . Calculate the molecular weight of the substance. (K_b for acetone is 17.2° per 100 gm.)

$$\begin{aligned} m &= \frac{100 K_b w}{W \Delta T} \\ &= \frac{100 \times 17.2 \times 2.5}{75 \times 0.43} \\ &= 133.3 \end{aligned}$$

B. Chemical Methods. The chemical methods described below are applicable only if the substance is either an acid or a base.

(i) **Silver Salt Method.** This method, applicable in the case of organic acids only, is based on the fact that the silver salts of organic acids are insoluble and are readily decomposed on ignition leaving behind a residue of metallic silver. The basicity of the acid should be known.

Procedure. A suitable amount of the acid is dissolved in an excess of dilute ammonia. The excess of ammonia is removed by boiling and then a slight excess of silver nitrate solution is added. The precipitate consisting of the silver salt is washed and dried. A known weight of the salt is heated carefully in a crucible to a constant weight. The residue left in the crucible is pure metallic silver.

Calculations. Suppose w gm. of silver salt on decomposition leaves a residue of silver weighing x gm.

$$\text{Now } \frac{\text{Equivalent weight of silver salt}}{\text{Equivalent weight of silver}} = \frac{\text{Wt. of silver salt}}{\text{Wt. of silver}}$$

$$\therefore \text{Equivalent weight of silver salt} = \frac{w}{x} \times 108 = M \text{ (say)}$$

$$\begin{aligned}\text{Equivalent weight of the acid} &= M - 108 + 1 = M - 107 \\ \therefore \text{Molecular weight of the acid} &= \text{Equivalent weight} \times \text{Basicity} \\ &= (M - 107) \times n\end{aligned}$$

where n is the basicity of the acid

Example 5. 0.700 gm. of the silver salt of a dibasic organic acid left on ignition 0.497 gm. of silver. Calculate the molecular weight of the acid.

$$\begin{aligned}\text{Weight of silver salt} &= 0.700 \text{ gm.} \\ \text{Weight of silver} &= 0.497 \text{ gm.} \\ \frac{\text{Equivalent weight of silver salt}}{\text{Equivalent weight of silver}} &= \frac{\text{Weight of silver salt}}{\text{Weight of silver}} \\ \therefore \text{Equivalent weight of silver salt} &= \frac{0.700 \times 108}{0.497} = 152.1 \\ \therefore \text{Equivalent weight of the acid} &= 152.1 - 108 + 1 = 45.1 \\ \therefore \text{Molecular weight of the acid} &= 45.1 \times 2 = 90.2\end{aligned}$$

(ii) **Chloroplatinic Salt Method.** This is applicable in the case of organic bases only. It is based on the fact that the organic bases, viz., amines, combine with chloroplatinic acid, H_2PtCl_6 , to form insoluble double salts known as platinichlorides or chloroplatinates. These salts have the general formula $\text{B}_2\text{H}_2\text{PtCl}_6$ where B stands for one equivalent of the base. On heating, they decompose leaving a residue of platinum.



$$\begin{aligned}\text{Molecular weight of the salt} &= 2B + 2 + 195 + 213 \\ &= 2B + 410\end{aligned}$$

where B is the equivalent weight of the base.

Thus $(2B + 410)$ gm. of the salt when ignited leaves 1 gm. atom of platinum as the residue.

or, $(2B + 410)$ gms. of the double salt $\equiv 195$ gm. of Pt

Suppose w gm. of the double salt is ignited and x gm. of the platinum residue is left behind.

$$\begin{aligned}\text{Now, } x \text{ gm. of Pt} &\equiv w \text{ gm. of the double salt} \\ \text{But } 195 \text{ gm. of Pt} &\equiv \text{Molecular weight of the double salt}\end{aligned}$$

$$\text{or} \quad \frac{x}{195} = \frac{w}{\text{Mol. wt. of the double salt}}$$

$$\therefore \text{Molecular weight of the double salt} = \frac{195 \times w}{x} = M(\text{say})$$

$$\therefore 2B + 410 = M$$

$$\text{or} \quad B = \frac{M - 410}{2}$$

if n is the acidity of the base, molecular weight of the base $= B \times n$

Example 6. 0.400 gm. of the platinichloride of a monoacid base gave on ignition 0.125 gm. of platinum. Calculate the molecular weight of the base.

Weight of the platinichloride (w) = 0.400 gm.

Weight of platinum residue (x) = 0.125 gm.

Let B represent one equivalent of the base.

\therefore Molecular formula of the platinichloride is $B_2H_2PtCl_6$ and

$$\text{Molecular weight of the plantinichloride} = \frac{0.400 \times 195}{0.125}$$

$$= 624$$

$$2B + 410 = 624$$

or

$$\text{or } B = \frac{624 - 410}{2} = 107$$

Thus, equivalent weight of the base = 107

Since it is monoacid. molecular weight = 107

Example 7. The chloroplatinate of a diacid base contains 40 per cent platinum. What is (a) the equivalent weight (b) the molecular weight of the base.

Let the weight of chloroplatinate = 100 gm.

Then the weight of platinum = 40 gm.

Let B represent one equivalent of the base.

\therefore Molecular formula of the chloroplatinate = $B_2H_2PtCl_6$

$$\text{Molecular weight of the chloroplatinate} = \frac{100}{40} \times 195 = 487.5$$

$$2B + 410 = 487.5$$

or

$$B = \frac{487.5 - 410}{2} = \frac{77.5}{2} = \text{Eq. wt. of the base}$$

Acidity = 2

$$\therefore \text{Molecular weight} = \frac{77.5}{2} \times 2 = 77.5$$

(iii) **Volumetric Method.** This method is applicable in the case of acids as well as bases. In order to determine molecular weight of an acid, a known weight of it is dissolved in water or alcohol and titrated against a standard alkali solution using phenolphthalein as indicator.

Calculations. Suppose w gm. of a dibasic acid requires 20 ml. of $N/10$ NaOH.

Then 20 ml. of $N/10$ NaOH $\equiv w$ gm. of acid

or 1000 ml. of $N/10$ NaOH $\equiv \frac{w}{20} \times 1000$ gm. of acid

or 1000 ml. of $N.$ NaOH $\equiv \frac{w}{20} \times 1000 \times 10$ gm. of acid
= 500 w gm. of acid

Since one equivalent of an acid requires 1000 ml. of *N.* alkali,

∴ Equivalent weight of the acid = 500 *w*

and Molecular weight of the acid = 500 *w* × Basicity
= 500 *w* × 2

Example 8. 0.25 gm. of an acid required 20.0 ml. of *N/10* KOH for neutralisation. Find out the equivalent weight of the acid. What will be the molecular weight of the acid if it is monobasic?

20.0 ml. of *N/10* KOH \equiv 0.25 gm of the acid

∴ 1000 ml. of *N.* KOH $\equiv \frac{0.25 \times 10 \times 1000}{20}$ gm. of the acid

= 125 gm. of the acid

But 1000 ml. of *N* alkali \equiv Equivalent weight of the acid

∴ Equivalent weight of the acid = 125

Basicity = 1

∴ Molecular weight = Equivalent weight × Basicity
= 125

Example 9. 0.250 gm. of an organic base required 15.0 ml. of *N/5* HCl for complete neutralisation. What is the molecular weight of the base if it is diacid?

15.0 ml. of *N/5* HCl \equiv 0.25 gm. of the base

∴ 1000 ml. of *N.* HCl $\equiv \frac{0.25 \times 5 \times 1000}{15}$ gm. of the base

= 83.3 gm. of the base

But 1000 ml. of normal acid = equivalent weight of the base

∴ Equivalent weight of the base = 83.3

Since, acidity = 2

∴ Molecular weight of the base = 166.6

Example 10. 0.50 gm. of a tribasic organic acid was dissolved in water and the volume made up to 100 ml. 10 ml. of this solution required 24.6 ml. of *N/20* NaOH for neutralisation. Calculate the molecular weight of the acid.

10 ml. of the acid \equiv 24.6 ml. of *N/20* NaOH

Let N_1 be the normality of the acid solution.

∴ $10 \times N_1 \equiv 24.6 \times \frac{1}{20}$

or $N_1 = \frac{24.6}{20 \times 10} = 0.123$

∴ Gm./litre of the acid = 0.123 × Eq. wt.

But actually gm./litre of the acid = $\frac{0.5}{100} \times 1000 = 5$

∴ 0.123 × Eq. wt. of the acid = 5

$$\begin{aligned} \text{or} \quad \text{Eq. wt. of the acid} &= \frac{5}{0.123} = 40.65 \\ \therefore \quad \text{Molecular weight} &= 40.65 \times 3 = 121.95 \end{aligned}$$

QUESTIONS

1. Describe briefly the various methods used for the determination of molecular weights of organic substances.

2. Describe the physical methods for the determination of molecular weight of organic substances.

3. Describe the chemical methods for the determination of molecular weight of organic acids and bases.

4. Describe in detail the Victor Meyer's method for the determination of molecular weight of a volatile substance.

0.1130 gm. of a substance on vaporization displaced 45.9 c.c. of air at 14°C and 754 mm. pressure. Calculate the molecular weight of the substance. (Aqueous tension at 14°C is 12.7 mm.) (Ans. 59.40)

5. 1.25 gm. of a substance was dissolved in 90 gm. of water when the solution was found to freeze at -0.25°C . Calculate the molecular weight of the substance. (K_f for benzene is 18.0°C). (Ans. 103.3)

6. 2.23 gm. of a non-volatile solute was dissolved in 100 gm. of benzene when the boiling point was raised by 0.466°C . Calculate the molecular weight of the solute. (K_b for benzene is 25.7°C). (Ans. 128.5)

7. The silver salt of a monobasic acid was found to contain 35 per cent silver. Calculate the molecular weight of acid. (Ans. 201.6)

8. 0.468 gm. of the platinichloride of a mono-acid base gave on ignition 0.1170 gm. of platinum. Calculate the molecular weight of the base. (Ans. 175)

9. 0.061 gm. of a dibasic acid required 10 ml. of decinormal NaOH solution for complete titration. Find out the molecular weight of the base. (Ans. 122)

10. 1.25 gm. of a monobasic acid was dissolved in water and the volume made upto 250 ml. 10 ml. of the solution required 7.5 ml. of N/12 NaOH. Calculate the molecular weight of the acid. (Ans. 80.0)

11. Relate the methods used specially for the determination of the molecular weights of organic acids and bases. (Panjab Inter. 1956)

12. How would you proceed to determine the molecular weight of an organic acid by silver salt method? (Panjab Inter. 1959 Suppl.)

13. 0.4 gm. of silver salt of a dibasic organic acid on ignition gave a residue of 0.284 gm. of metallic silver. Find the molecular weight of the acid. (Ans. 90.2) (Panjab Inter. 1961 Suppl.)

14. Explain how would you proceed to determine the equivalent weight of an organic acid supplied to you.

1.026 gm. of the silver salt of a tribasic organic acid on ignition gave 0.648 gm. of metallic silver. Calculate the molecular weight of the acid. (Ans. 192) (Panjab Inter. 1961. Suppl.)

15. The freezing point of the solution of 1.392 gm. of an organic acid (assumed to be undissociated in solution) in 20 gm. of water, was found to be -1.11°C (K for water -18.5°C). 0.177 gm. of the same acid neutralized exactly 15 ml. of 0.2 N alkali. Calculate the basicity of the acid. (Ans. 2) (Panjab Inter. 1953 Suppl.)

16. 0.8675 gm. of the chloroplatinate of a mono-acid base gave on ignition 0.3584 gm. of platinum. Find the molecular weight of the base. (Ans. 31.0)

(Panjab Inter. 1960 Suppl.)

17. With the help of a neat diagram, describe Victor Meyer's method for finding the molecular weight of a volatile liquid. (Panjab Inter. 1956. Suppl.)

18. 0.532 gm. of the platinichloride of a diacid organic base left 0.195 gm. of platinum on ignition. Calculate the molecular weight of the base. (Ans. 122)

(Panjab Inter. 1960)

19. 0.1693 gm. of a volatile substance was introduced in the Victor Meyer tube for determination of vapour density. It displaced 58.9 ml. of air at 27°C and 746 mm. pressure. Calculate the molecular weight of the substance. (Aqueous tension at $27^{\circ}\text{C} = 26.7$ mm.) (Ans. 74.74)

(Panjab Inter. 1960. Suppl.)

20. In a Victor Meyer's apparatus, 0.46 gm. of chloroform displaced 30.5 ml. of air measured over water at 22°C , the barometric pressure being 755 mm. Calculate the molecular weight of chloroform. (Aqueous tension at $22^{\circ}\text{C} = 20$ mm.)

(Ans. 376.5) (Panjab Inter. 1961 Suppl.)

CHAPTER XXII

DETERMINATION OF EMPIRICAL, MOLECULAR AND STRUCTURAL FORMULAE

After determining the percentage composition of an organic compound, the next step in the systematic investigation is to determine its empirical and molecular formulae.

Empirical Formula

The empirical formula of a compound is defined as the simplest formula expressing the relative number of atoms of each element present in one molecule of the compound. This can be calculated from the percentage composition of the compound.

The following steps are involved :

1. The percentage of each element is divided by the atomic weight of the element. This gives the relative number of atoms of the various elements present in the compound.

2. The lowest number obtained in the first step is selected. All other numbers are divided by this lowest number. The quotients are usually whole numbers. If not, they are reduced to whole numbers by multiplying with a suitable common factor.

Example 1. The percentage composition of an organic substance as determined by analysis was as below :

Carbon = 14.4%, Hydrogen = 1.8%, Chlorine = 64.6%, Calculate the empirical formula of the compound.

Element	Percentage	Relative No. of atoms (Percentage/At. wt.)	Dividing by the smallest factor	Simplest whole number ratio
Carbon	14.4	$\frac{14.4}{12} = 1.2$	1	2
Hydrogen	1.8	$\frac{1.8}{1} = 1.8$	1.5	3
Chlorine	64.6	$\frac{64.6}{35.5} = 1.8$	1.5	3
Oxygen	19.2 (By difference)	$\frac{19.2}{16} = 1.2$	1	2

∴ Empirical formula of the compound is $C_2H_3Cl_3O_2$

Example 2. 0.2025 gm. of an organic substance was found to give the following results on analysis :

Carbon dioxide = 0.5280 gm.

Nitrogen = 0.0210 gm.

Water = 0.1215 gm.

Find out the empirical formula of the compound (Karachi Inter. 1953)

(i) Determination of percentage composition. :

Weight of the substance taken = 0.2025 gm.

Weight of CO₂ formed = 0.5280 gm.

Weight of H₂O formed = 0.1215 gm.

Weight of nitrogen collected = 0.0210 gm.

$$\text{Percentage of carbon} = \frac{12}{44} \times 0.5280 \times \frac{100}{0.2025} = 71.11$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times 0.1215 \times \frac{100}{0.2025} = 6.66$$

$$\text{Percentage of nitrogen} = 0.0210 \times \frac{100}{0.2025} = 10.37$$

(ii) Determination of empirical formula :

Element	Percentage	Relative No. of atoms (Percentage/At.wt.)	Dividing by the smallest factor	Simplest whole number ratio
Carbon	71.11	$\frac{71.11}{12} = 5.92$	8.00	8
Hydrogen	6.66	$\frac{6.66}{1} = 6.66$	9.00	9
Nitrogen	10.37	$\frac{10.37}{14} = 0.74$	1.00	1
Oxygen	11.86 (By difference)	$\frac{11.86}{16} = 0.74$	1.00	1

∴ The empirical formula of the compound is C₈H₉NO

Example 3. 0.200 gm. of an organic compound containing carbon, hydrogen, nitrogen, and oxygen, gave on combustion 74.6 c.c. of nitrogen at N.T.P. In a second experiment 0.200 gm. yielded 0.147 gm. of carbon dioxide and 0.12 gm. of water. Find the empirical formula of the compound. (Panjab Inter. 1941)

(i) Determination of percentage composition :

(a) Weight of the substance taken = 0.200 gm.

Volume of nitrogen at N.T.P. = 74.6 c.c.

$$\therefore \text{Percentage of nitrogen} = \frac{28 \times 74.6}{22400 \times 0.200} \times 100 = 46.62$$

(b) Weight of the substance taken = 0.200 gm.

Weight of carbon dioxide formed = 0.147 gm.

Weight of water formed = 0.147 gm.

$$\therefore \text{Percentage of carbon} = \frac{12}{44} \times 0.147 \times \frac{100}{0.200} = 20.05$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times 0.120 \times \frac{100}{0.200} = 6.66$$

$$\text{Percentage of oxygen} = 100 - (46.62 + 20.05 + 6.66) = 26.67$$

(i) Determination of empirical formula :

Element	Percentage	Relative No. of atoms (Percentage/A.wt.)	Dividing by the smallest factor	Simplest whole number ratio
Carbon	20.05	$\frac{20.05}{12} = 1.67$	1.00	1
Hydrogen	6.66	$\frac{6.66}{1} = 6.66$	3.99	4
Nitrogen	46.62	$\frac{46.62}{14} = 3.33$	1.99	2
Oxygen	26.67	$\frac{26.67}{16} = 1.67$	1.00	1

\therefore The empirical formula of the compound is $\text{CH}_4\text{N}_2\text{O}$.

Example 4. 0.369 gm. of a compound containing carbon, hydrogen and bromine gave on combustion 0.396 gm. of carbon dioxide and 0.189 gm. of water. Also 0.246 gm. of the substance gave 0.379 gm. of silver bromide (Panjab Inter. 1955 S)
What is the formula of the substance?

(i) Determination of percentage composition :

(a) Weight of the substance taken = 0.369 gm.

Weight of CO_2 formed = 0.396 gm.

Weight of H_2O formed = 0.189 gm.

$$\therefore \text{Percentage of carbon} = \frac{12}{44} \times \frac{0.396 \times 100}{0.369} = 29.27$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times 0.189 \times \frac{100}{0.369} = 5.69$$

(b) Weight of the substance taken = 0.246 gm.

Weight of AgBr formed = 0.379 gm.

$$\therefore \text{Percentage of bromine} = \frac{80}{188} \times 0.379 \times \frac{100}{0.246} = 65.55$$

(ii) Determination of empirical formula :

Element	Percentage	Relative No. of atoms (Percentage/At. wt.)	Dividing by the smallest factor	Simplest whole number ratio
Carbon	29.27	$\frac{29.27}{12} = 2.437$	$\frac{2.437}{0.819} = 2.97$	3
Hydrogen	5.69	$\frac{5.69}{1} = 5.690$	$\frac{5.69}{0.819} = 6.95$	7
Bromine	65.55	$\frac{65.55}{80} = 0.819$	$\frac{0.819}{0.819} = 1.00$	1

∴ The empirical formula of the compound is C_3H_7Br .

Molecular Formula

The molecular formula of a compound expresses the *actual number of atoms of each element present in one molecule of the compound*.

Molecular formula may be the same as the empirical formula or simple multiple of it.

Suppose the empirical formula of a compound is CH_2O . Evidently, its empirical formula weight is $12 + 2 + 16 = 30$. Let the molecular weight of the compound be 60. Then the molecular formula will be $\frac{60}{30}$ times i.e., 2 times the empirical formula. Therefore, molecular formula is $C_2H_4O_2$.

Thus,

$$\text{Molecular formula} = \text{Empirical formula} \times n$$

$$\text{where } n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

Example 5. An organic substance contains 10.15 per cent carbon, 0.84 per cent hydrogen and 88.98 per cent chlorine.

1.20 gm. of the substance when vaporised occupied 225 ml. at N.T.P. Calculate the molecular formula of the compound.

(i) Determination of empirical formula :

Element	Percentage	Relative number of atoms (Percentage/At. wt.)	Dividing by the smallest factor	Simplest whole number ratio
Carbon	10.15	$\frac{10.15}{12} = 0.84$	1.0	1
Hydrogen	0.84	$\frac{0.84}{1} = 0.84$	1.0	1
Chlorine	88.98	$\frac{88.98}{35.5} = 2.51$	2.99	3

$$\therefore \text{Empirical formula} = \text{CHCl}_3$$

$$\text{Empirical formula weight} = 12 + 1 + 106.5 = 119.5$$

(i) **Determination of molecular weight :**

Weight of the substance = 1.20 gm.
 Volume of the vapour at N.T.P. = 225 ml.

$$\therefore \text{Molecular weight} = \frac{22400 \times 1.20}{225} = 119.5$$

(ii) **Determination of molecular formula :**

$$\therefore \text{Molecular formula} = \text{Empirical formula} \times \frac{\text{Mol. Wt.}}{\text{Emp. formula wt.}}$$

$$= (\text{CHCl}_3) \times 1 = \text{CHCl}_3$$

Example 6. On combustion, 0.200 gm. of a dibasic organic acid gave 0.04 gm. of H_2O and 0.195 gm. of CO_2 . It contained no nitrogen. When 0.500 gm. of its silver salt was ignited, it gave a residue of 0.355 gm. of metallic silver. Calculate the molecular formula of the acid. (Parjah Inter 1958)

(i) **Determination of percentage composition :**

Weight of the substance = 0.200 gm.
 Weight of CO_2 = 0.195 gm.
 Weight of H_2O = 0.040 gm.

$$\text{Percentage of carbon} = \frac{12}{44} \times 0.195 \times \frac{100}{0.200} = 26.59$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times 0.04 \times \frac{100}{0.200} = 2.22$$

$$\therefore \text{Percentage of oxygen} = 100 - (26.59 + 2.22) = 71.19$$

(ii) **Determination of empirical formula :**

Element	Percentage	Relative number of atoms (Percentage/At. wt.)	Dividing by the smallest factor	Simplest whole num- ber ratio
Carbon	26.59	$\frac{26.59}{12} = 2.22$	1.00	1
Hydrogen	2.22	$\frac{2.22}{1} = 2.22$	1.00	1
Oxygen	71.19	$\frac{71.19}{16} = 4.45$	2.01	2

$$\therefore \text{Empirical formula} = \text{CHO}_2$$

$$\text{Empirical formula weight} = 12 + 1 + 32 = 45$$

(iii) **Determination of molecular weight :**

Weight of the silver salt = 0.500 gm.
 Weight of silver = 0.355 gm.

$$\frac{\text{Equivalent weight of silver salt}}{\text{Equivalent weight of silver}} = \frac{\text{Weight of silver salt}}{\text{Weight of silver}}$$

$$\therefore \text{Equivalent weight of silver salt} = \frac{0.500}{0.355} \times 108$$

$$= 152.1$$

$$\therefore \text{Equivalent weight of the acid} = 152.1 - 108 + 1$$

$$= 45.1$$

$$\text{Basicity} = 2$$

$$\therefore \text{Molecular weight of the acid} = 90.2$$

(iv) Determination of molecular formula.

$$\text{Molecular formula} = \text{Empirical formula} \times \frac{\text{Mol. wt.}}{\text{Emp. formula wt.}}$$

$$= (\text{CHO}_2) \times \frac{90.2}{45} = \text{C}_2\text{H}_2\text{O}_4$$

Example 7. 0.45 gm. of monobasic organic acid gave on combustion 1.136 gm. of CO_2 and 0.1992 gm. of H_2O . 0.500 gm. of the silver salt of the same acid left on ignition 0.2358 gm. of silver. Find out the molecular formula of the acid.

(i) Determination of percentage composition :

$$\text{Weight of the acid} = 0.45 \text{ gm.}$$

$$\text{Weight of } \text{CO}_2 = 1.136 \text{ gm.}$$

$$\text{Weight of } \text{H}_2\text{O} = 0.1992 \text{ gm.}$$

$$\therefore \text{Percentage of carbon} = \frac{12}{44} \times 1.136 \times \frac{100}{0.45} = 68.85$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times 0.1992 \times \frac{100}{0.45} = 4.92$$

$$\therefore \text{Percentage of oxygen} = 100 - (68.85 + 4.92) = 26.23$$

(ii) Determination of empirical formula :

Element	Percentage	Relative number of atoms (Percentage/At. wt)	Dividing by the smallest factor	Simplest whole number ratio
Carbon	68.85	$\frac{68.85}{12} = 5.74$	3.50	7
Hydrogen	4.92	$\frac{4.92}{1} = 4.92$	3.0	6
Oxygen	26.23	$\frac{26.23}{16} = 1.64$	1.0	2

$$\therefore \text{Empirical formula} = \text{C}_7\text{H}_6\text{O}_2$$

$$\text{Empirical formula weight} = 84 + 6 + 32 = 122$$

(iii) Determination of molecular weight :

$$\frac{\text{Equivalent weight of silver salt}}{\text{Equivalent weight of silver}} = \frac{\text{Weight of silver salt}}{\text{Weight of silver}}$$

$$\therefore \text{Equivalent weight of silver salt} = \frac{0.500 \times 108}{0.2358} = 229.0$$

$$\therefore \text{Equivalent weight of the acid} = 229.0 - 108 + 1$$

$$= 122$$

$$\text{Basicity} = 1$$

$$\therefore \text{Molecular weight of the acid} = 122$$

(iv) Determination of molecular formula :

$$\text{Molecular formula} = \text{Empirical formula} \times \frac{\text{Mol. wt.}}{\text{Emp. formula wt.}}$$

$$= (\text{C}_7\text{H}_6\text{O}_2) \times \frac{122}{122} = \text{C}_7\text{H}_6\text{O}_2$$

Example 8. A mono-acid organic base gave the following results on analysis :

- (i) 0.150 gm. gave 0.4323 gm. CO_2 and 0.1134 gm. H_2O .
- (ii) 0.200 gm. gave 20.7 c.c. nitrogen at 0°C and 760 m.m. pressure.
- (iii) 0.44 gm. of the chloroplatinate left on ignition 0.1375 gm. of platinum.

Calculate the molecular formula of the base.

(i) Determination of percentage composition :

$$\text{Weight of the substance} = 0.150 \text{ gm.}$$

$$\text{Weight of } \text{CO}_2 = 0.4323 \text{ gm.}$$

$$\text{Weight of } \text{H}_2\text{O} = 0.1134 \text{ gm.}$$

$$\therefore \text{Percentage of carbon} = \frac{12}{44} \times 0.4323 \times \frac{100}{0.15} = 78.60$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times 0.1134 \times \frac{100}{0.15} = 8.40$$

$$(b) \text{ Weight of substance} = 0.200 \text{ gm.}$$

$$\text{Volume of nitrogen at } 0^\circ\text{C and 760 mm. pressure}$$

$$\text{i.e., the volume at N.T.P.} = 20.7 \text{ ml.}$$

$$\therefore \text{Percentage of nitrogen} = \frac{28 \times 20.7 \times 100}{22400 \times 0.200} = 12.93$$

(ii) Determination of empirical formula.

Element	Percentage	Relative number of atoms (Percentage/At. wt.)	Dividing by the smallest factor	Simplest whole number ratio
Carbon	78.60	$\frac{78.6}{12} = 6.55$	7.12	7
Hydrogen	8.40	$\frac{8.40}{1} = 8.40$	9.1	9
Nitrogen	12.93	$\frac{12.93}{14} = 0.92$	1.0	1

\therefore Empirical formula is C_7H_9N

Empirical formula weight = $84 + 9 + 14 = 107$

(iii) Determination of molecular weight :

Weight of the chloroplatinate = 0.44 gm.

Weight of platinum = 0.1375 gm.

Let B represent one equivalent of the base.

Molecular formula of the chloroplatinate = $B_2H_2PtCl_6$

\therefore Molecular weight of the chloroplatinate = $\frac{0.44 \times 195}{0.1375} = 624$

or $2B + 410 = 624$

$\therefore B = 107$

\therefore Equivalent weight of the base = 107

Acidity = 1

\therefore Molecular weight of the base = 107

(iv) Determination of molecular formula :

Molecular formula = Empirical formula $\times \frac{\text{Mol. wt.}}{\text{Emp. formula wt.}}$
 $= (C_7H_9N) \times 1 = C_7H_9N$

Example 9. An organic monobasic acid was analysed as follows :

(a) 0.1935 gm. gave 0.1320 gm. CO_2 and 0.0270 gm. H_2O .

(b) It contained 55.04% chlorine.

(c) 0.2709 gm. of the acid dissolved in water neutralized 20.2 ml. of $N/12$ NaOH.

Calculate the empirical formula and molecular formula of the acid.

(i) Determination of percentage composition :

Weight of the acid = 0.1935 gm.

Weight of CO_2 = 0.1320 gm.

Weight of H_2O = 0.0270 gm.

$$\therefore \text{Percentage of carbon} = \frac{12}{44} \times 0.1320 \times \frac{100}{0.1935} = 18.61$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times 0.0270 \times \frac{100}{0.1935} = 1.55$$

$$\text{Percentage of chlorine (given)} = 55.04$$

(ii) Determination of empirical formula :

Element	Percentage	Relative number of atoms (Percentage At. wt)	Dividing by the smallest factor	Simplest whole number ratio
Carbon	18.61	$\frac{18.61}{12} = 1.55$	1.0	1
Hydrogen	1.55	$\frac{1.55}{1} = 1.55$	1.0	1
Chlorine	55.04	$\frac{55.04}{35.5} = 1.55$	1.0	1
Oxygen	24.80 By difference	$\frac{24.80}{16} = 1.55$	1.0	1

$$\therefore \text{Empirical formula} = \text{CHClO}$$

$$\text{Empirical formula weight} = 12 + 1 + 35.5 + 16 = 64.5$$

(iii) Determination of molecular weight :

$$25.2 \text{ ml. of N/12 NaOH} \equiv 0.2709 \text{ gm. of the acid}$$

$$\therefore 1000 \text{ ml. of N.NaOH} \equiv \frac{0.2709 \times 12 \times 1000}{25.2} = 129.0 \text{ gm. of the acid}$$

$$\therefore \text{Equivalent weight of the acid} = 129.0$$

$$\text{Basicity} = 1$$

$$\therefore \text{Molecular weight} = 129.0$$

(iv) Determination of molecular formula :

$$\text{Molecular formula} = \text{Empirical formula} \times \frac{\text{Mol. wt.}}{\text{Emp. formula wt}}$$

$$= \text{CHClO} \times 2 = \text{C}_2\text{H}_2\text{Cl}_2\text{O}_2$$

Example 10. A dibasic organic acid gave the following results on analysis :

0.2496 gm. of the acid gave 0.3168 gm. CO_2 and 0.0864 gm H_2O

0.1092 gm. of the acid was exactly neutralised by 21.0 ml. of N/10 NaOH .

Calculate the molecular formula of the acid. (Panjab Inter 1962)

(i) Determination of percentage composition :

Weight of the acid = 0.2496 gm.

Weight of CO_2 = 0.3168 gm.Weight of H_2O = 0.0864 gm.

$$\therefore \text{Percentage of carbon} = \frac{12}{44} \times 0.3168 \times \frac{100}{0.2496} = 34.61$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times 0.0864 \times \frac{100}{0.2496} = 3.84$$

$$\text{Percentage of oxygen (by difference)} = 61.55$$

(ii) Determination of empirical formula :

Element	Percentage	Relative number of atoms (Percentage/At.wt.)	Dividing by the smallest factor	Multiplying by 3	Simplest whole number ratio
Carbon	34.61	$\frac{34.61}{12} = 2.88$	1.00	3.00	3
Hydrogen	3.84	$\frac{3.84}{1} = 3.84$	1.33	3.99	4
Oxygen	61.55 (by diff.)	$\frac{61.55}{16} = 3.85$	1.33	3.99	4

 \therefore Empirical formula is $\text{C}_3\text{H}_4\text{O}_4$ Empirical formula wt. = $36 + 4 + 64 = 104$

(iii) Determination of molecular weight :

21.0 ml. of $N/10$ NaOH \equiv 0.1092 gm. of the acid

$$\therefore 1000 \text{ ml. of } N \text{ NaOH} \equiv \frac{0.1092 \times 10 \times 100}{21.0} = 52.00 \text{ gm. of the acid.}$$

Equivalent weight of the acid = 52.00
Basicity = 2

Molecular weight of the acid = 104.00

(iv) Determination of molecular formula :

$$\begin{aligned} \text{Molecular formula} &= \text{Empirical formula} \times \frac{\text{Mol. wt.}}{\text{Emp. formula wt.}} \\ &= \text{C}_3\text{H}_4\text{O}_4 \times 1 \\ &\quad \text{C}_3\text{H}_4\text{O}_4 \end{aligned}$$

Example 11. The empirical formula of a monobasic acid is CH_2O . The vapour density of its ethyl ester is found to be 44. Calculate the molecular formula of the acid.

Empirical formula = CH_2O \therefore Empirical formula weight = $12 + 2 + 16 = 30$

$$\begin{aligned}
 &\text{Vapour density of the ethyl ester} = 44 \\
 \therefore &\text{Molecular weight of ethyl ester} = 88 \\
 \text{i.e., Molecular weight of } R\cdot\text{COOC}_2\text{H}_5 &= 88 \\
 \therefore &\text{Molecular weight of } R\cdot\text{COOH} = 88 - 29 + 1 = 60 \\
 &= \text{CH}_2\text{O} \times \frac{60}{30} = \text{C}_2\text{H}_4\text{O}_2 \\
 \therefore &\text{Molecular formula}
 \end{aligned}$$

Structural Formula

After determining molecular formula of a compound, the next step is to ascertain its *structural* or *constitutional* formula which gives the manner in which the various atoms are arranged within the molecule. This information can be obtained by studying chemical reactions of the compound.

A few examples are given below. They will be more readily understood after the student has gone through the properties of organic compounds of different categories in the succeeding chapters.

Example 12. Determine the molecular as well as structural formulae of a compound from the following data :

(a) It contains $C = 16.27\%$; $H = 0.68\%$, $Cl = 72.20\%$.

(b) 0.2950 gm. of it displaced in a Victor Meyer's apparatus 50.46 ml of moist air at 24°C and 753.7 mm. pressure.

(c) It forms addition product with sodium bisulphite and yields chloroform when warmed with caustic soda solution. (Aq. tension at $24^\circ\text{C} = 22.2$ m.m.) (Panjab Inter 1950)

(i) Percentage composition. It is given that :

$C = 16.27$; $H = 0.68$; $Cl = 72.20$, $O = 10.85$ (by difference).

(ii) Calculation of empirical formula :

Element	Percentage	At. wt.	$\frac{\text{Percentage}}{\text{At. wt.}}$	Dividing by smallest factor
C	16.27	12	1.36	2
H	0.68	1	0.68	1
Cl	72.20	35.5	2.03	3
O	10.85	16	0.68	1

\therefore Empirical formula = $\text{C}_2\text{HCl}_3\text{O}$

(iii) Calculation of molecular weight :

Weight of the substance taken = 0.2950 gm. •

Volume, $V_2 = 50.46$ ml. ; Pressure, $P_2 = 753.7 - 22.2 = 731.5$ mm.

Temperature, $T_2 = 273 + 24 = 297^\circ\text{A}$

$$\begin{aligned}
 \frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} \\
 \frac{760 \times V_1}{273} &= \frac{731.5 \times 50.46}{297}
 \end{aligned}$$

$$\text{or } V_1 = \frac{731.5 \times 50.46 \times 273}{760 \times 297} = 44.64 \text{ ml.}$$

Now 44.64 ml. of vapour at *N.T.P.* weigh 0.295 gm.

\therefore 22,400 ml. of vapour at *N.T.P.* weigh

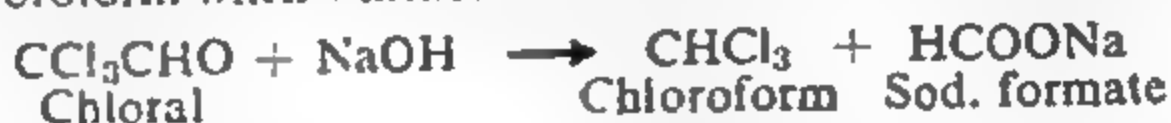
$$= \frac{0.295 \times 22400}{44.64} = 148.2 \text{ gm.}$$

Hence molecular weight = 148.2

Empirical formula weight = $24 + 1 + 106.5 + 16 = 147.5$

Hence molecular formula is the same as the empirical formula, i.e. $\text{C}_2\text{HCl}_3\text{O}$.

(iv) **Structural formula.** Since the compound forms an addition product with sodium bisulphite, it may have an aldehyde group. Therefore, the compound has the structure CCl_3CHO which is chloral. This is confirmed by the fact that the compound yields chloroform when warmed with caustic soda solution:



Example 13. (i) 0.1800 gm. of an organic substance gave on combustion 0.4693 gm. of carbon dioxide and 0.1080 gm. of water.

(ii) 100 gm. of the substance contained 10.37 gm. of nitrogen. Determine the empirical formula of the substance.

If molecular weight of the substance is 135 and on hydrolysis it yields acetic acid and a primary amine which is diazotisable, assign structural formula to it. (Panjab Inter. 1951 S)

(i) **Calculation of percentage composition :**

$$\text{C} = \frac{12}{44} \times 0.4693 \times \frac{100}{0.18} = 71.11\%$$

$$\text{H} = \frac{2}{18} \times 0.108 \times \frac{100}{0.18} = 6.67\%$$

$$\text{N} = 10.37\%$$

$$\text{O} = 11.85\% \text{ (By difference)}$$

(ii) **Calculation of empirical formula :**

Element	Percentage	At. Wt.	$\frac{\text{Percentage}}{\text{At. wt.}}$	Dividing by smallest factor
C	71.11	12	5.93	8
H	6.67	1	6.67	9
N	10.37	14	0.74	1
O	11.85	16	0.74	1

Empirical formula $\rightarrow \text{C}_8\text{H}_9\text{NO}$

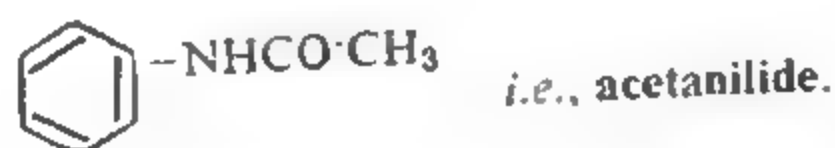
Empirical formula weight = $96 + 9 + 14 + 16 = 135$

(iii) **Determination of molecular formula.**

$$\text{Molecular formula} = \text{Empirical formula} \times \frac{\text{Mol. wt.}}{\text{Emp. formula wt.}}$$

$$\text{C}_8\text{H}_9\text{NO} \times 1 = \text{C}_8\text{H}_9\text{NO}$$

(iv) **Structural formula.** Since the compound on hydrolysis yields a primary amine (which is diazotisable) and acetic acid, its structural formula appears to be



It undergoes hydrolysis as shown below :



Example 14. 0.369 gm. of a yellowish organic liquid on combustion gave 0.792 gm. of carbon dioxide and 0.135 gm. of water vapour. It contained 11.4 percent of nitrogen. Its molecular weight was 123. Its reduction product on warming with chloroform and alcoholic potash gave a vapour with disgusting odour. What was the liquid? (Panjab Inter. 1952)

(i) Calculation of percentage composition :

$$\text{Carbon} = \frac{12}{44} \times 0.792 \times \frac{100}{0.369} = 58.53\%$$

$$\text{Hydrogen} = \frac{2}{18} \times 0.135 \times \frac{100}{0.369} = 4.06\%$$

$$\text{Nitrogen} = 11.40\%$$

$$\text{Oxygen} = 26.01\% \quad (\text{By difference})$$

(ii) Calculation of empirical formula. :

Element	Percentage	At. wt.	Percentage At. Wt.	Dividing by smallest factor.
C	58.53	12	4.88	6
H	4.06	1	4.06	5
N	11.40	14	0.81	1
O	26.01	16	1.63	2

\therefore Empirical formula is $\text{C}_6\text{H}_5\text{NO}_2$

Empirical formula weight = 123

(iii) Determination of molecular formula :

$$\text{Molecular formula} = \text{Empirical formula} \times \frac{\text{Mol. wt.}}{\text{Emp. formula wt.}}$$

$$= \text{C}_6\text{H}_5\text{NO}_2 \times \frac{123}{123} = \text{C}_6\text{H}_5\text{NO}_2$$

(iv) **Structural formula.** This compound appears to be nitrobenzene as nitrobenzene on reduction yields aniline (a primary amine), which on treatment with chloroform and alcoholic potash gives vapour with disgusting odour (carbylamine reaction).

The compound itself, therefore, should be nitrobenzene, having the structural formula



Example 15. An organic acid has the percentage composition : C = 26.4% : H = 2.2% , O = 71.4%. The acid is dibasic and its silver salt contains 71.1 per cent of silver. What is the molecular formula of the acid? It is readily oxidised by KMnO_4 and is decomposed by sulphuric acid to give carbon dioxide and carbon monoxide. What is the structural formula? (J. and K. Inter. 1957)

(i) Calculation of empirical formula :

Element	Percentage	At. Wt.	$\frac{\text{Percentage}}{\text{At. wt.}}$	Dividing by smallest factor
C	26.4	12	2.2	1
H	2.2	1	2.2	1
O	71.4	16	4.4	2

\therefore Empirical formula is CHO_2

Empirical formula weight = 45

(ii) Calculation of molecular weight :

Weight of silver salt = 100.0 gm.

Weight of silver = 71.1 gm.

Equivalent weight of silver salt = $\frac{100.0}{71.1} \times 108 = 152.11$

\therefore Equivalent weight of the acid = $152.11 - 108 + 1 = 45.11$

\therefore Molecular weight of the acid = $45.11 \times 2 = 90.22$

(iii) Determination of molecular formula :

$$\begin{aligned} \text{Molecular formula} &= \text{Empirical formula} \times \frac{\text{Mol. wt.}}{\text{Emp. formula wt.}} \\ &= \text{CHO}_2 \times \frac{90.22}{45.11} = \text{C}_2\text{H}_2\text{O}_4 \end{aligned}$$

(iv) Structural formula. Since the substance is a dibasic acid, it seems to be



This is confirmed by the facts that :

(i) it is oxidised by KMnO_4 readily and

(ii) with sulphuric acid it gives CO_2 and CO .

Example 16. A dibasic organic acid gave the following results on analysis : 0.2496 gm. of the acid gave 0.4168 gm. CO_2 and 0.0864 gm H_2O . 0.1092 gm. of the acid was exactly neutralised by 20.0 ml. of N/10 NaOH solution. Calculate the molecular formula of the acid and also write down its structural formula. (Panjab Inter 1955 S)

(i) Calculation of percentage composition :

$$C = \frac{1}{44} \times 0.4163 \times \frac{100}{0.2496} = 45.54\%$$

$$H = \frac{2}{18} \times 0.0864 \times \frac{100}{0.2496} = 3.85\%$$

$$O = 50.61\% \text{ (by difference)}$$

(ii) Calculation of empirical formula :

Element	Percentage	At. Wt.	Percentage At. Wt.	Dividing by smallest factor
C	45.54	12	3.79	1.2
H	3.85	1	3.85	1.3
O	50.61	16	3.16	1

\therefore Empirical formula = CHO

Empirical formula weight = 29

(iii) Calculation of molecular weight :

\therefore 21.0 ml. N/10 NaOH neutralises 0.1092 gm. of acid

\therefore 1000 ml. N NaOH neutralises $0.1092 \times 1000 \times \frac{10}{21.0} = 52$ gm. of acid

\therefore Equivalent wt. = 52

Basicity = 2

\therefore Molecular weight = Eq.wt. \times basicity
= $52 \times 2 = 104$

(iv) Calculation of molecular formula :

Molecular formula = Empirical formula $\times \frac{\text{Mol. wt.}}{\text{Emp. formula wt.}}$

$$= \text{CHO} \times \frac{104}{29} = \text{C}_4\text{H}_4\text{O}_4$$

(v) Structural formula. Since it is a dibasic acid, the structural formula of the compound $\text{C}_4\text{H}_4\text{O}_4$ will be



i.e. Maleic acid

Example 17. A monoacid primary amine contains 53.3 per cent carbon, 15.6 per cent hydrogen and 31.1 per cent nitrogen. 0.1087 gm. of its platinic salt gave 0.0424 gm. of platinum on ignition. Calculate the molecular formula and name the compound. (J. and K. Inter. 1958)

(i) Calculation of empirical formula :

Element	Percentage	At. Wt.	$\frac{\text{Percentage}}{\text{At. Wt.}}$	Dividing by Smallest factor
C	53.3	12	4.44	2
H	15.6	1	15.60	7
N	31.1	14	2.22	1

\therefore Empirical formula = $\text{C}_2\text{H}_7\text{N}$

Empirical formula weight = 45

(ii) Calculation of molecular weight :

Weight of the platonic salt of the compound = 0.1087 gm.

Wt. of platinum left on ignition = 0.0424 gm.

Let B represent one equivalent of the base,

\therefore Molecular formula of the platonic salt is $B_2\text{H}_2\text{PtCl}_6$
and molecular weight of the platonic chloride,

$$= \frac{0.1087 \times 195}{0.0424}$$

$$= 500$$

Or $2B + 410 = 500$

$\therefore B = \frac{500 - 410}{2} = 45$

Thus, equivalent weight of the amine = 45

Since it is a monoacid amine, molecular weight = 45

(iii) Calculation of Molecular formula :

$$\text{Molecular formula} = \text{Empirical formula} \times \frac{\text{Mol. wt.}}{\text{Emp. formula wt.}}$$

$$\therefore \text{C}_2\text{H}_7\text{N} \times \frac{45}{45} = \text{C}_2\text{H}_7\text{N}$$

(4) Name of compound. Since it is a monoacid primary amine, it must contain H_2 group. Therefore, the compound is ethylamine, i.e., $\text{C}_2\text{H}_5\text{NH}_2$.

Molecular Formulae of Hydrocarbons. For details of the method and some numerical questions on molecular formulae of hydrocarbons see VIII.

QUESTIONS

1. Find the empirical formula. How is it determined? An organic compound contains 75 per cent carbon, 6.6 per cent hydrogen and remaining is oxygen. Calculate the empirical formula of the compound. (Ans. CH_2O)

2. An organic compound containing carbon, hydrogen, nitrogen and oxygen gave the following results :

Carbon = 49.32 per cent ; hydrogen = 9.58 per cent and nitrogen = 19.18 per cent. Calculate the empirical formula of the compound. (Ans. $\text{C}_3\text{H}_7\text{NO}$)

3. 0.45 gm. of an organic compound gave on combustion 0.99 gm. of carbon dioxide and 0.54 gm. of H_2O . Find out the simplest formula of the compound. (Ans. $\text{C}_3\text{H}_8\text{O}$)

4. 0.1502 gm. of a compound on treatment in Dumas' method yielded 25.4 ml. of moist nitrogen measured at 14°C and 760 mm. pressure. 0.3050 gm. gave on combustion 0.5670 gm. CO_2 and 0.1932 gm. H_2O .
Calculate empirical formula of the compound. Aqueous tension at 14°C may be taken as 12.8 mm. (Ans. $\text{C}_5\text{H}_5\text{NO}$)

5. 0.1772 gm. of an organic compound containing carbon, hydrogen, nitrogen and oxygen gave on combustion 0.2638 gm. CO_2 and 0.1345 gm. H_2O . 0.296 gm. of the same compound was kjeldahlised when the ammonia evolved required 49.5 ml. of 0.1N hydrochloric acid for neutralization. Calculate the empirical formula of the compound. (Ans. $\text{C}_2\text{H}_3\text{NO}$)

6. 0.90 gm. of an organic compound gave on combustion, 0.6 gm. CO_2 and 0.54 gm. of H_2O . The ammonia evolved on kjeldahlising 0.412 gm. was absorbed in 50 c.c. of N/5 H_2SO_4 and the excess of the acid required 34.00 c.c. of N/10 NaOH . Calculate the empirical formula of the compound. (Ans. CH_4NO_2)
(Panjab Inter 1948)

7. 0.1800 gm. of an organic substance gave on combustion 0.4693 gm. CO_2 and 0.1080 gm. H_2O .
100 gm. of the substance contained 10.37 gm. of combined nitrogen. Determine the empirical formula of the substance. (Ans. $\text{C}_8\text{H}_9\text{NO}$) (Panjab Inter 1951)

8. One gram. of an organic compound known to contain carbon, hydrogen, nitrogen and oxygen required 33.4 c.c. of normal sulphuric acid for the neutralization of ammonia formed in a Kjeldahl's experiment.

On complete combustion, 0.500 gm. of the compound gave 0.366 gm. of CO_2 and 0.299 gm. of H_2O . Calculate the percentage composition of the compound and give its empirical formula. (Ans. C=19.6% ; H=6.66% ; N=46.76% ; O=26.62% ; Empirical formula is $\text{CH}_4\text{N}_2\text{O}$) (Panjab Inter. 1958 Suppl.)

9. A dibasic organic acid gave the following results on analysis : 0.2496 gm. of acid gave 0.3168 gm. CO_2 and 0.0864 gm. H_2O . 0.1092 gm. of the acid was exactly neutralised by 21.0 c.c. of N/10 NaOH . Calculate the molecular formula of the acid. (Ans. $\text{C}_3\text{H}_4\text{O}_4$) (Panjab Inter 1952, 1955)

10. An organic liquid, on analysis, gave the following results :

- Element ; C, H, N, O.
- On combustion C was found to be 41.37 per cent and H to be 5.75 per cent.
- On kjeldahlising 1.01 gm. of the substance the ammonia evolved neutralised 11.6 ml. of N.HCl.
- 0.1015 gm. of the liquid when vaporised displaced 27.96 ml. of dry air measured at 15°C and 750 mm. pressure. Find the true formula of the acid. (Ans. $\text{C}_3\text{H}_5\text{NO}_2$) (Panjab Inter. 1961 Suppl.)

11. 0.30 gm. of an organic compound containing C, H, N and O gave the following results on analysis :

0.5214 gm. of CO_2 ; 0.1206 gm. of H_2O ; N 10.4%. Its molecular weight was found to be 135. On boiling with dil H_2SO_4 it gave aniline and acetic acid. Assign a structural formula to the compound (Ans. $\text{C}_8\text{H}_9\text{NO}$; $\text{CH}_3\text{CONHC}_6\text{H}_5$) (Panjab Inter 1960 Suppl.)

12. On combustion 0.20 gm. of a dibasic organic acid gave 0.195 gm. CO_2 and 0.04 gm. H_2O . 0.500 gm. of its silver salt gave on ignition 0.355 gm. of silver. Find the molecular formula of the acid. (Ans. $\text{C}_2\text{H}_2\text{O}_4$) (Panjab Inter. 1958; 1945)

13. A sweet smelling readily combustible organic liquid analysed as under : 0.432 gm. on combustion gave 0.405 gm. of water and 0.99 gm. of carbon dioxide. When evaporated in a Victor Meyer tube, 0.21 gm. of it displaced 96.9 c.c. of air collected over water at 27°C and 746.5 mm. pressure. (Aqueous tension at 27°C = 26.5 mm)

The liquid forms (i) a crystalline solid with sodium bisulphite and (ii) gives a red colour on treating with concentrated solution of sodium nitroprusside and then adding NaOH solution dropwise. What was the liquid and why ?

(Ans. $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{CH}_3 \end{array}$, acetone) (Panjab Inter. 1954 Suppl.)

14. An organic liquid on analysis yielded the following results :

- (a) Elements present. C, H, N and S
- (b) On combustion C and H were found to be 41.37% and 5.73% respectively.
- (c) On kjeldahlising, the ammonia obtained from 1.01 gm. of the substance was neutralised by 11.6 ml. of N. HCl.
- (d) In the Carius estimation of sulphur, 0.2066 gm. of the substance resulted in the precipitation of 0.5544 gm. of BaSO_4 .
- (e) 0.1015 gm. of the liquid when vaporised displaced 27.96 ml. of dry air measured at 15°C and 750 mm. pressure.

Find the true formula of the substance (Ans. $\text{C}_3\text{H}_5\text{NS}$) (Panjab Inter 1945)

15. 0.369 gm. of a yellowish organic liquid on combustion produced 0.792 gm. of CO_2 and 0.135 gm. of water. Nitrogen estimation revealed 11.4% of the element.

0.135 gm. of the liquid in a Victor Meyer apparatus displaced 28.5 c. c. of air collected over water at 27°C and 743.5 mm. pressure.

Its reduction product on warming with chloroform and alcoholic potash produced a vapour with a disgusting odour. What was the liquid ? Aqueous tension at $27^\circ\text{C}=23.5$ mm.

(Ans. $\text{C}_6\text{H}_5\text{NO}_2$) (Panjab Inter 1952)

16. Find the empirical and molecular formula of a dibasic acid from the following data.

- (a) 0.3192 gm. of the acid gave on combustion 0.4224 gm. of CO_2 and 0.1512 gm. of H_2O .
- (b) It contained 10.52% nitrogen.
- (c) The vapour density of its dimethyl ester is 80.50.

(Ans. $\text{C}_4\text{H}_7\text{NO}_4$) (Panjab Inter. 1950)

17. Determine the molecular as well as the structural formula of a compound from the following data :

- (a) It contained C=16.27%; H=0.68%; Cl=72.20%
- (b) 0.2950 gm. of it displaced in a Victor Meyer's apparatus, 50.64 ml. of moist air at 24°C and 753.7 mm. pressure.

It forms addition product with sodium bisulphite and yields chloroform when warmed with caustic soda solution. Aqueous tension at $24^\circ\text{C}=22.2$ mm.

(Ans. CCl_3CHO) (Panjab Inter. 1950)

18. An organic dibasic acid contains C=17.39% H=1.45% and Br=57.97%. Vapour density of its normal ethyl ester is 166. Determine the empirical and molecular formula of the acid.

(Ans. $\text{C}_4\text{H}_4\text{O}_2\text{Br}$) (Panjab Inter 1949)

19. 0.10 gm. of an organic monobasic acid gave on combustion 0.505 gm of CO_2 and 0.0892 gm of H_2O .

1.5 gm of the acid required 15 c.c. of N/10 NaOH for complete neutralization. Determine the molecular formula of acid.

(Ans. $\text{C}_7\text{H}_9\text{O}_2$) (Panjab Inter 1945)

20. A mono acid organic base gave the following results on analysis :

(a) 0.100 gm. gave 0.2882 gm. CO_2 and 0.0756 gm. H_2O .

(b) 0.200 gm. gave 21.8 c.c. of dry nitrogen at 15°C and 760 mm. pressure

(iii) 0.400 gm. of the platinichloride left on ignition 0.125 gm. of platinum. What is the molecular formula of the base? (Ans. C_7H_9N) (Panjab Inter. 1949)

21. A dibasic acid containing only C, H and O was found to contain C = 26.7 and H = 2.2%. The vapour density of its diethyl ester was found to be 73. What is the acid? (Ans. $(COOH)_2$) (Jammu & Kashmir 1954)

22. (i) 0.2905 gm. of a solid organic acid on combustion gave 0.6160 gm. of CO_2 and 0.0944 gm. of H_2O .

(ii) On heating with soda lime, its sodium salt gave benzene.

(iii) It forms two series of salts and two series of esters.

(iv) It furnishes an anhydride on simple heating; find the structural formula of the acid. (Ans. $C_6H_4(COOH)_2$) (Panjab Inter 1951)

23. (a) Describe briefly the gravimetric method of determining the molecular weight of organic bases

(b) 0.596 gm. of platinichloride of a monoacid organic base left on ignition 0.195 gm. of platinum. Calculate the molecular weight of the base and also give the name of this aromatic amine. (Ans. 93, Aniline) (Panjab T.D.C. Part I, 1963)

24. (a) Give briefly the methods for the detection and estimation of sulphur in an organic compound.

(b) 0.477 gm. of the silver salt of a dibasic organic acid gave on ignition 0.324 gm. of metallic silver. Calculate the molecular weight of the acid. (Ans. 104) (Panjab T.D.C., Part I, 1964)

25. Explain briefly 'Silver salt' method for the determination of the molecular weight of an organic acid. 0.075 gm. of a monobasic organic acid required 10 ml. of N/12 NaOH for complete neutralisation. Find the molecular weight of the acid. (Ans. 90) (Panjab T.D.C. Part I, 1964 S)

26. A monoacid organic base gave the following results on analysis:

(a) 0.100 gm. gave 0.1812 gm. CO_2 and 0.0756 gm. water.

(b) 0.200 gm. gave 21.8 cc. of Nitrogen measured at $15^\circ C$ and 760 mm.

(c) 0.300 gm. of the Platini chloride left on ignition 0.09375 gm. of Platinum.

What is the Molecular Formula of the base?

(Panjab T.D.C. (I) 1966)

(Ans. C_7H_9N)

27. A mono acid base gave the following results on analysis:—

0.2 gm. gave 0.5764 gm. of carbon dioxide and 0.1512 gm. water.

0.3 gm. of the base gave 32.7 ml. nitrogen at $15^\circ C$. and 760 mm. pressure.

0.535 gm. of the base required 12.5 ml. of N/2.5 hydrochloric acid for complete neutralisation.

What is the molecular formula of the base?

(Ans. C_7H_9N) (Panjab Pre. Engg & Med. 1966)

CHAPTER XXIII

CHEMICAL LINKAGES, MOLECULAR STRUCTURE AND ISOMERISM

Cause of Chemical Combination. As is now well-known, *the real cause of chemical combination lies in tendency of the atoms to complete their outermost orbits.* The atoms of the inert gases, except helium, contain 8 electrons in their outermost orbits. Helium which has only one orbit contains 2 electrons. Since the inert gases have no tendency for chemical combination, it is believed that their outermost orbits are complete. It follows, therefore, that the outermost orbit of an atom is complete when it has 8 electrons. The outermost orbit of hydrogen, however, is complete when it has 2 electrons (*cf.* helium).

Now atoms of all elements (other than the inert gases) have incomplete outer orbits. They have, therefore, a tendency to combine under suitable conditions. During such combinations there is a rearrangement of electrons in such a way that each atom acquires 8 electrons in its outermost orbit.

The rearrangement takes place by any one of the following two ways :

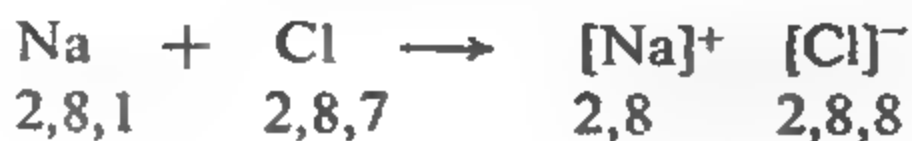
(i) By the *transference* of one or more electrons from one atom to the other.

(ii) By the *sharing* of electrons between the two atoms.

Types of Linkages. Three types of linkages are known :

Electrovalent Linkage. *The linkages established by the transference of one or more electrons from one atom to another is known as electrovalent linkage and the compound formed is termed as electrovalent or ionic compound.*

For example, the formation of sodium chloride. Sodium (configuration 2, 8, 1) loses one electron and chlorine (configuration 2, 8, 7) gains that electron and thus both acquire 8 electrons in their outermost orbits :

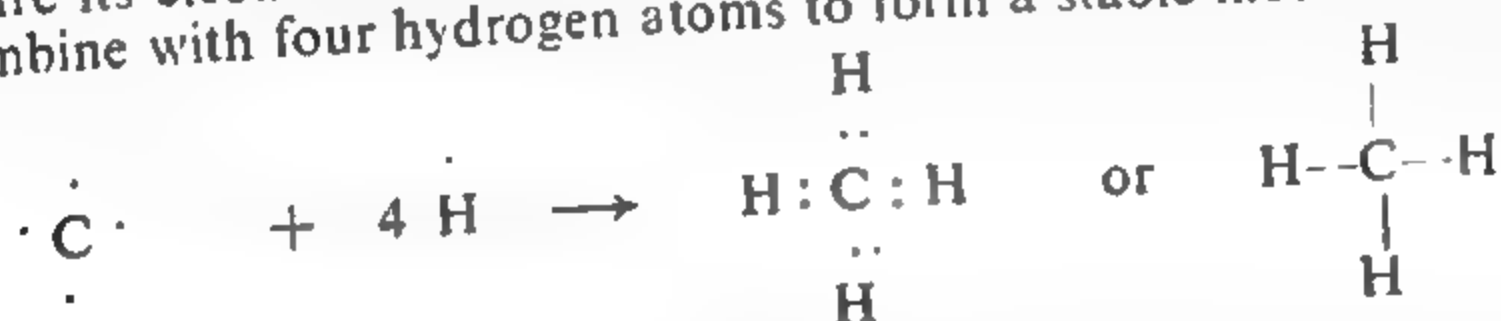


Sodium atom loses one electron and, therefore, bears a unit positive charge while chlorine atom gains it and, therefore, bears a unit negative charge. These charged particles are called ions.

The electrovalent compounds conduct electricity in fused state as well as in aqueous solution. They are largely soluble in water and only slightly soluble in organic solvents. They have rather high melting and boiling points.

B. Covalent Linkage. The linkage established by the sharing of electrons between two atoms is known as covalent linkage and the compound formed is termed as covalent compound.

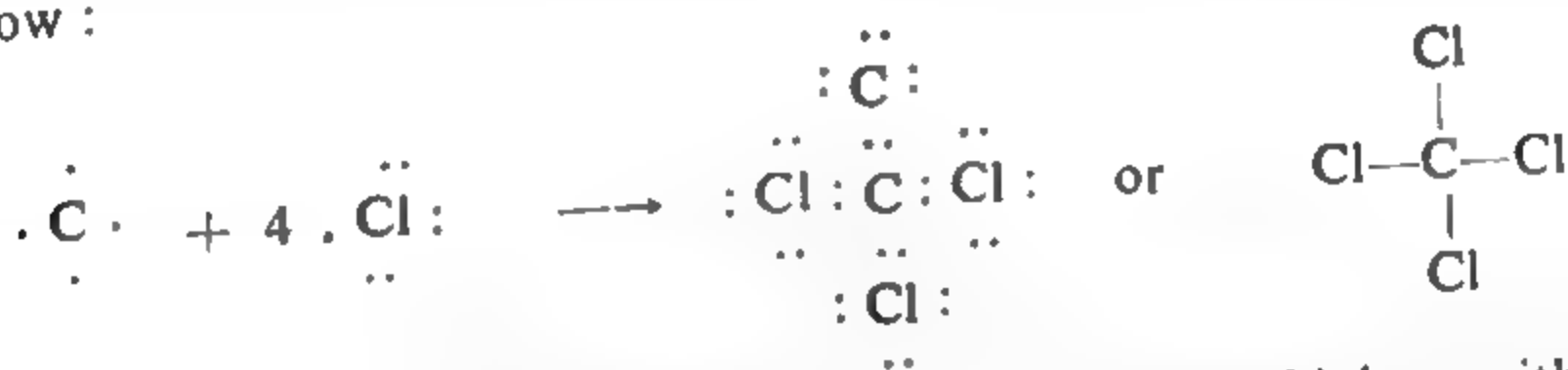
Most of the carbon compounds (*i.e.*, organic compounds) are formed by covalent linkages. The reason is that the carbon atom has four electrons in the outer orbit. It can neither lose all these electrons nor can gain four additional electrons to acquire stable configuration. But it can share its electrons with other elements. Thus, one carbon atom can combine with four hydrogen atoms to form a stable molecule of methane.



The carbon atom acquires 8 electrons in its outermost orbit while each of the hydrogen atoms acquires two electrons.

Thus, the bond between each carbon and hydrogen atom is covalent which is usually represented by a single dash as has been done in the above formula of methane. The covalency of carbon is seen to be four while that of hydrogen is one. It is useful to remember that a single bond, as above, represents a pair of shared electrons.

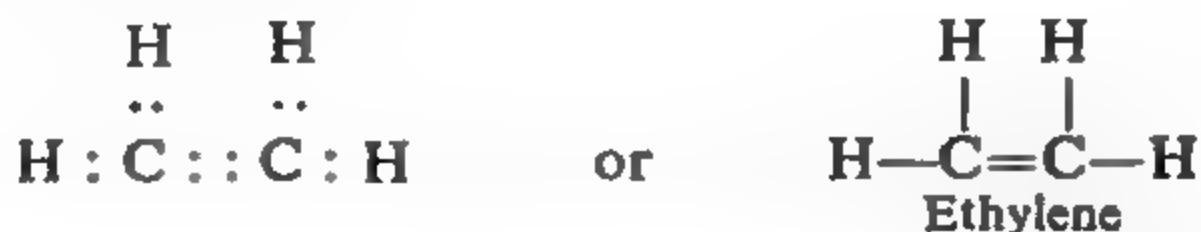
The combination of carbon with chlorine (which has seven electrons in the outermost orbit) to form carbon tetrachloride is represented as below :



Carbon atom has remarkable property of combining with other carbon atoms by the similar process of sharing of electrons. Thus, two carbon atoms may be joined by the sharing of one pair of electrons between them. The octet round each carbon atom may be completed by sharing electrons with three hydrogens as shown below in the formation of ethane :



Double Bond. If the carbon atoms are joined together by the *sharing of two pairs of electrons* instead of one (as in the above case), the bond between them is said to be a **double bond**. This may be represented as below in case of ethylene :



A compound containing $\text{C}=\text{C}$ bond is said to be **unsaturated**. The representation of this bond by double linkage does not, by any means imply that the bond is 'stronger' than the single bond. Actually, the presence of double bond in a compound makes it less stable, that is, more reactive because there is always a tendency for a double bond to convert itself into a single bond. The double bond in ethylene, for example readily changes into a single bond on treatment with hydrogen or bromine.

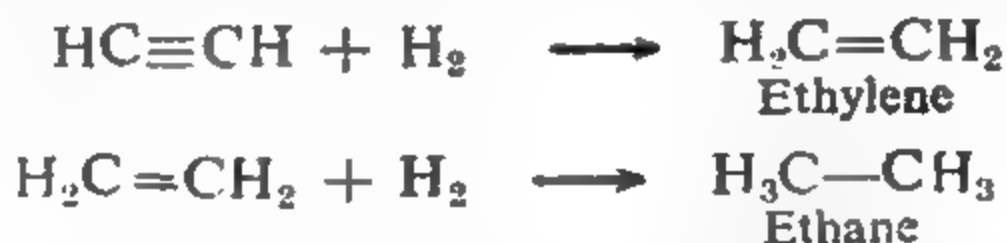


These reactions are known as **addition reactions**. The full significance of the double bond has been explained in Chapter XXIII.

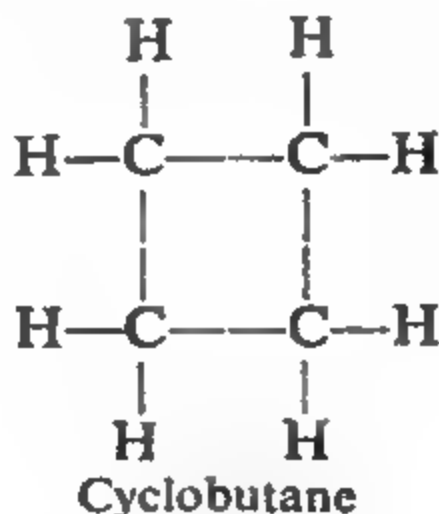
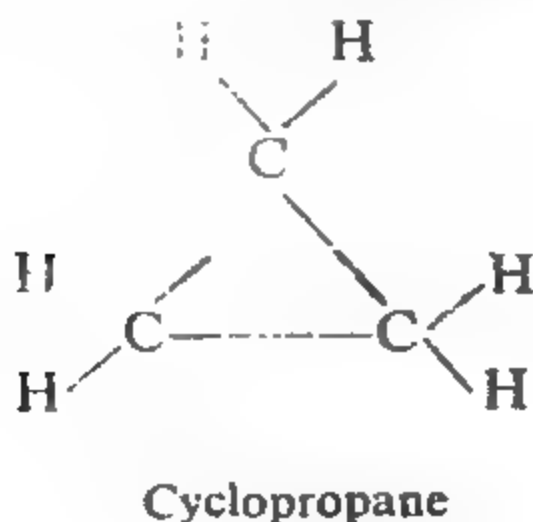
Triple Bond. If two carbon atoms are joined together by the *sharing of three pairs of electrons*, the bond between them is said to be a **triple bond**. This type of linkage may be represented as,



The presence of triple bond in a compound makes it even more reactive as there is even greater tendency to acquire a single bond. Thus, acetylene readily changes into ethane on treatment with hydrogen.



Formation of Rings. Carbon atoms may be joined to one another not only in chains (as shown above in the case of ethane, ethylene and acetylene) but also in rings as shown below :



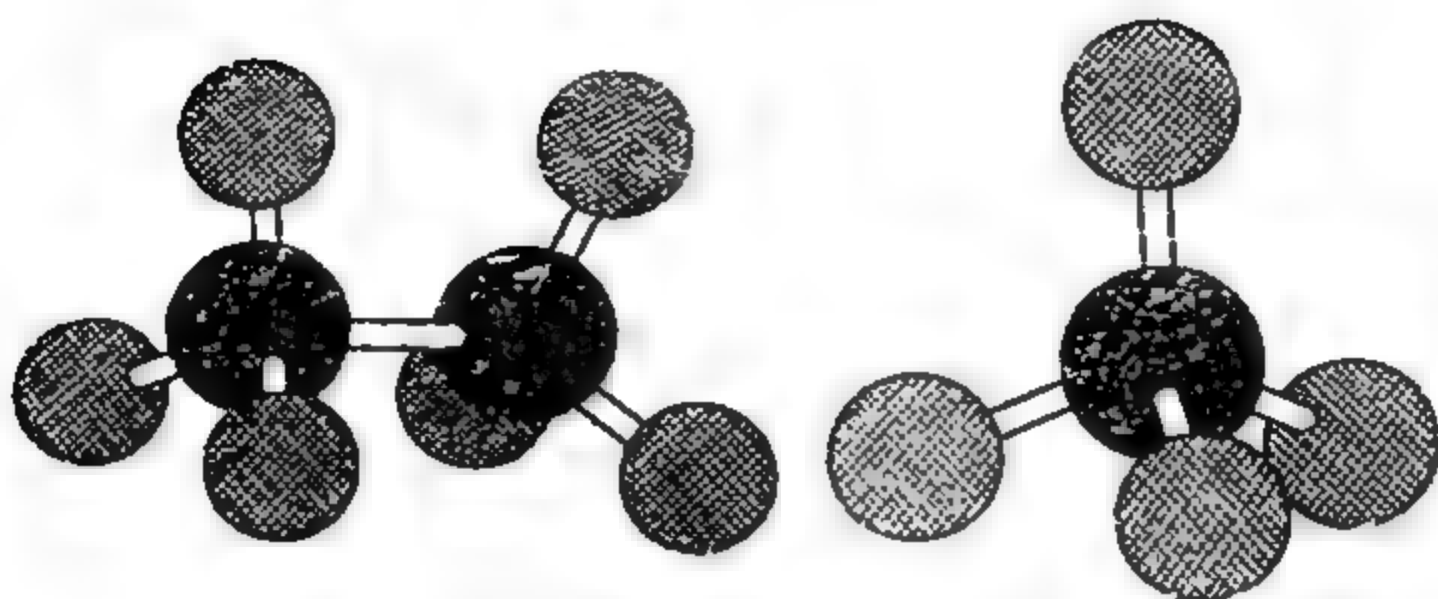
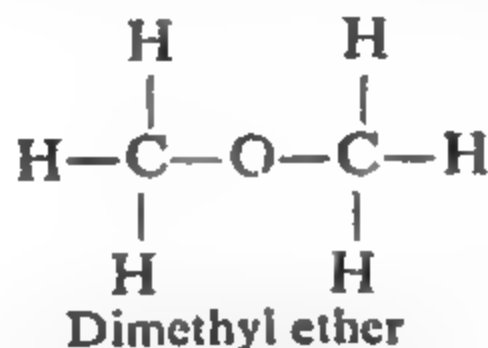
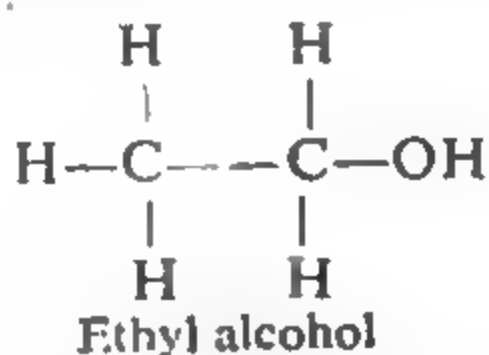


Fig. 2. Space models of methane and ethane

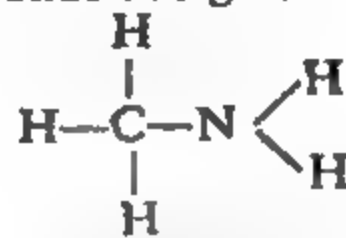
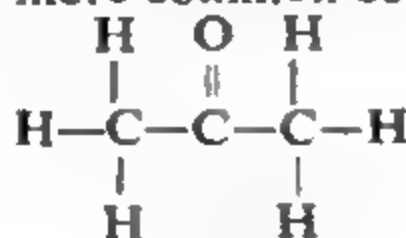
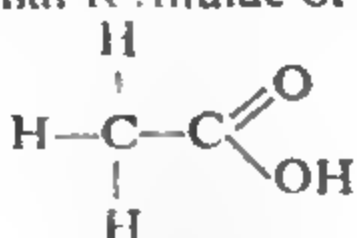
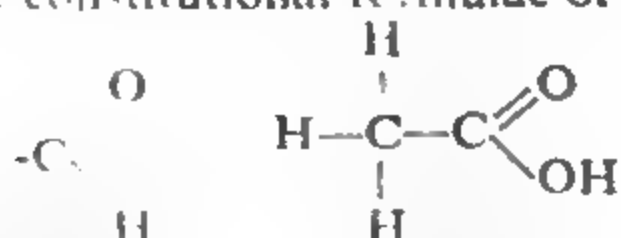
Structural Formula

As pointed out earlier, a simple molecular formula, C_2H_6O , represents two different compounds, ethyl alcohol (C_2H_5OH) and dimethyl ether (CH_3OCH_3) which have entirely different properties. There are several other such instances which have been discussed under isomerism in this chapter. It is evident, therefore, that although the common elements, carbon, hydrogen, oxygen, etc., have definite valencies, there can be more than one way in which their definite numbers can be joined together. Therefore, the organic chemist was confronted with a new problem, unknown in organic chemistry, of representing two or more compounds having the same molecular formula in a manner which may readily be understood. Thus, ethyl alcohol and dimethyl ether are represented as :



These formulae are called **structural** or **constitutional** or **graphic formulae**.

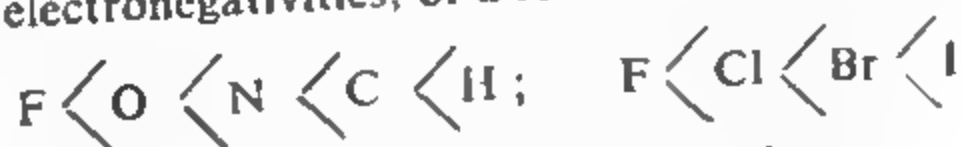
The constitutional formulae of a few more common compounds are given below:



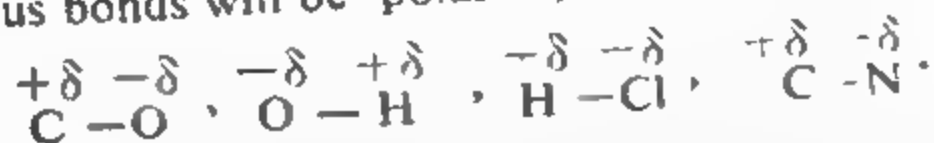
Partial Polar Character of the Covalent Bond. Perhaps it may be assumed that a covalent bond is completely a *non-ionic* bond as the shared pair of electrons may be supposed to be symmetrically distributed between the two atoms concerned. The fact is, however, different.

Very often, especially when two dissimilar atoms are involved in a covalent bond, the charge of the shared pair of electrons is displaced more towards one atom than the other, which develops a small polarity on the two atoms; that is, one of the atoms acquires a fractional +ve charge ($+\delta$) and the other a fractional -ve charge ($-\delta$). Which of the two atoms acquires the -ve charge or the +ve charge depends upon the relative *electro negativities* of the two atoms. *The electronegativity is defined as the power of the atom to attract electron towards itself.*

The order of electronegativities, of a few elements is given below :



Thus various bonds will be polar as, for example,



Evidently, the magnitude of the charge δ , will differ in each case.

The above considerations are confirmed by what is known as the dipole moment of various compounds containing the above bonds.

Isomerism. As mentioned above, in organic chemistry there are many cases where a given molecular formula represents two or more compounds which differ in physical as well as chemical properties. Such compounds which have the same molecular formula but differ from one another in physical and chemical properties are said to be isomers or isomerides and the phenomenon is known as isomerism.

There are two main types of isomerism.

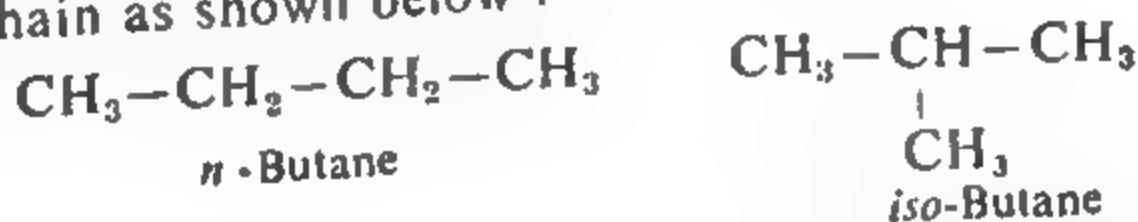
(A) Structural Isomerism

(B) Stereoisomerism

(A) **Structural Isomerism.** Structural isomerism is that which is due to the difference in the arrangement of the atoms within the molecule. In other words, the difference in each isomer arises from the method of linking of the atoms, without any reference to their position in space.

Structural isomerism is of four kinds :

(a) **Chain Isomerism.** This kind of isomerism is due to the difference in the structure of the carbon chain. Thus, normal butane and iso-butane, both having the molecular formula, C_4H_{10} , differ in the manner of linking of the chain as shown below :

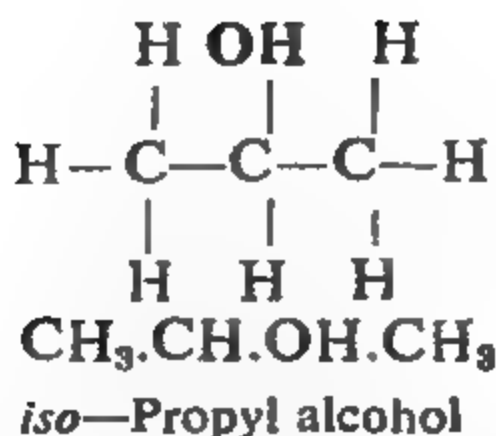
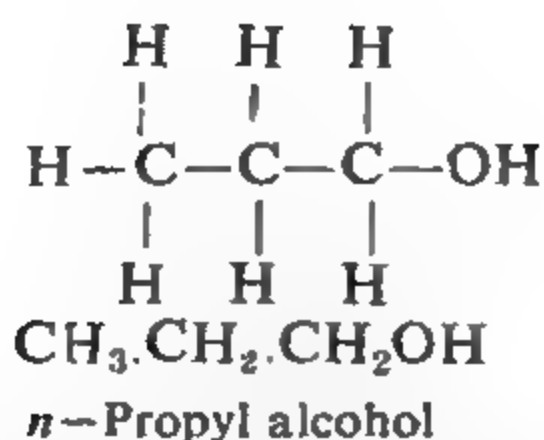


Similarly, two ethers of the formula $C_4H_{10}O$ are known. They are diethyl ether and methyl propyl ether :



As the number of carbon atoms increases in a molecule, the number of possible structural isomers also increases. Thus, there are two butanes (C_4H_{10}), three pentanes (C_5H_{12}), five hexanes (C_6H_{14}), nine heptanes (C_7H_{16}) and so on.

(b) **Position Isomerism.** Position isomerism arises from the difference in the position occupied by a particular atom or a group. Thus, normal propyl alcohol and isopropyl alcohol, both having the same formula, C_3H_7OH , differ in the relative position of the hydroxyl group in each molecule :



(c) **Functional Isomerism.** This kind of isomerism is due to the presence of different functional groups in the compounds having the same molecular formula. For example,



have the same molecular formula but while the former contains ether group ($-\text{O}-$) the latter contains the hydroxyl group ($-\text{OH}$). Another example is,

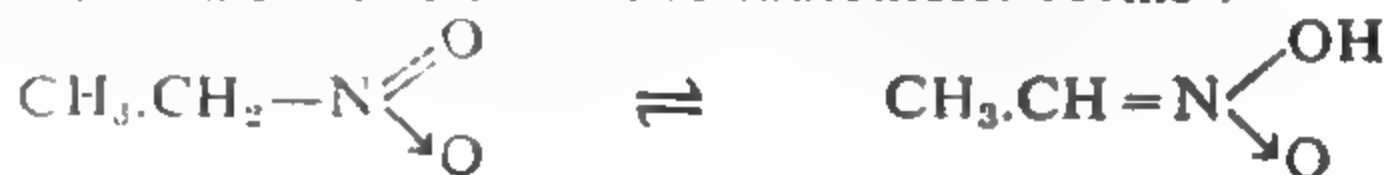


(d) **Tautomerism.** This type of isomerism involves a compound which can exist simultaneously in two forms in equilibrium with each other. For example, hydrocyanic acid exists in two forms in equilibrium :



The form $\text{H}-\text{C}\equiv\text{N}$ usually predominates.

Nitroethane also exists in two tautomeric forms :



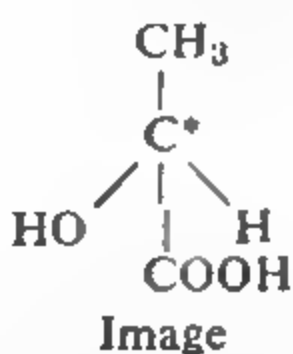
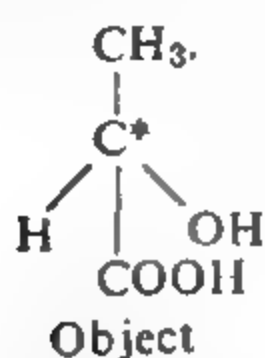
It will be seen that tautomerism involves the shifting of the position of a hydrogen atom. Such a hydrogen atom is known as "mobile" hydrogen.

(e) **Stereoisomerism or Space Isomerism.** This type of isomerism is due to the difference in the spatial positions of the atoms in the molecule. It arises, although the atoms are linked in the same way in each molecule, the difference arises from the way in which the atoms are arranged in space. Such isomers are known as **stereoisomers**.

Two types of stereoisomerism is known.

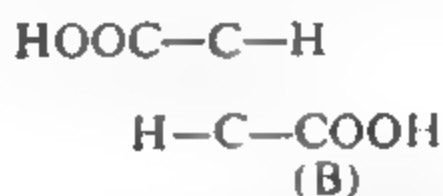
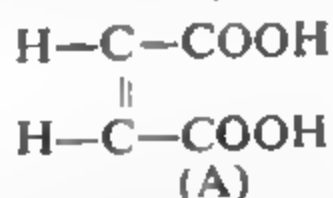
- (a) *Optical* (b) *geometrical*

In *optical isomerism*, the isomers differ from each other only in respect of their behaviour towards the polarised light. One of them rotates the plane of the polarised light towards the right (*dextro rotation*) and the other towards the left (*levo rotation*). This difference becomes clear if it is realised that the configurations of the two molecules are mirror image of each other ; for example, in lactic acid $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, we have



The *geometrical isomerism* arises due to fact that positions of atoms or groups linked to two carbon atoms across a double bond become fixed in space, because a double bond somehow restricts free rotation of groups within the molecule.

Thus two structures (A) and (B) are possible for the constitutional formula HOOC.HC=CH.COOH , and these are



In fact both these are known. Structure A represents maleic acid and B is fumaric acid. This is the most well known example of geometrical isomerism. Numerous other examples of stereoisomerism are also known. (For more details, an advanced organic text may be consulted).

Significance of Double Bond

Baeyer's strain theory. According to van't Hoff, the four valencies of a carbon atom are directed towards the four corners of a regular tetrahedron, as explained earlier, and the angle between any two valencies (linkages) is $109^\circ 28'$ (Fig. 3). If this angle is varied in the formation of a certain compound, a strain is set up in the resulting molecule. The greater the variation from the normal angle, the greater is the strain. The linkage of two carbon atoms by a single bond does not interfere

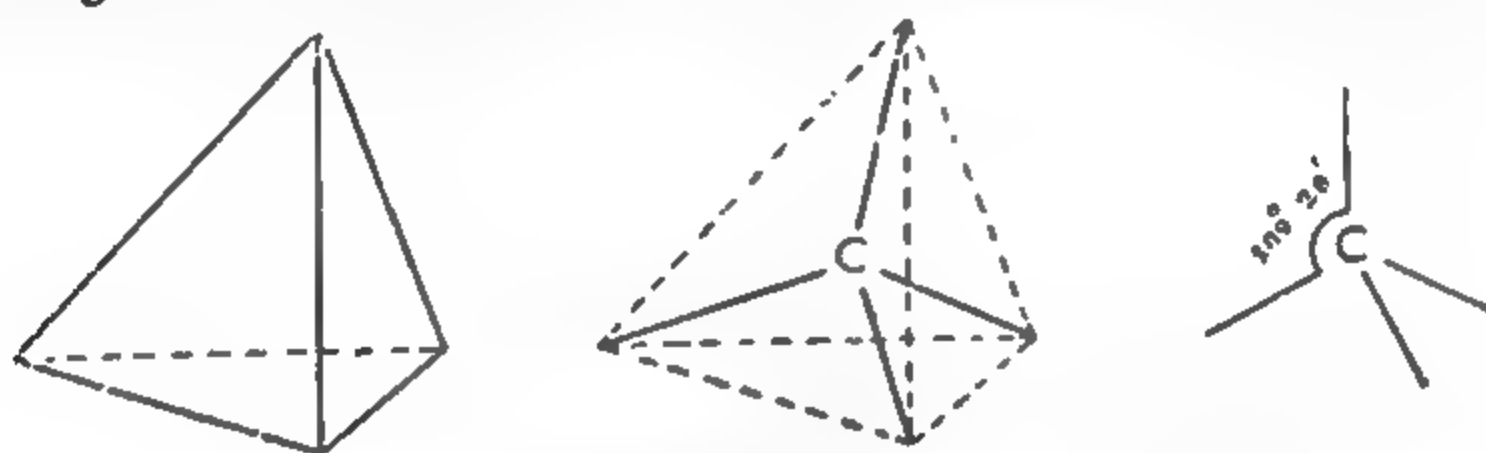


Fig. 3. Tetrahedral structure of carbon atom.

with the normal angle and hence no strain is produced. The single bond is, therefore, strong and stable. But the linkage of two carbon atoms by a

double bond, as in ethylene $\begin{array}{c} \text{H} \quad \text{H} \\ \backslash \quad / \\ \text{C}=\text{C} \\ / \quad \backslash \\ \text{H} \quad \text{H} \end{array}$, results in a considerable

displacement of the valency bonds. The bonds now become nearly parallel (Fig. 4) and, therefore, the angle between them becomes



Fig. 4. Valency bonds in ethylene molecule

zero. The angle through which each bond has been displaced, evidently is $\frac{109^{\circ}28' - 0}{2} = 54^{\circ}44'$. Thus, the formation of a double bond involves a very heavy distortion or strain in the molecule. Consequently, the compound is not stable.

The strain can only be relieved when the $C=C$ bond is converted into $C-C$ bond. The compound has a strong tendency, therefore, to open and form addition products as illustrated in Fig. 5. The addition of bromine to ethylene molecule takes place readily resulting in the

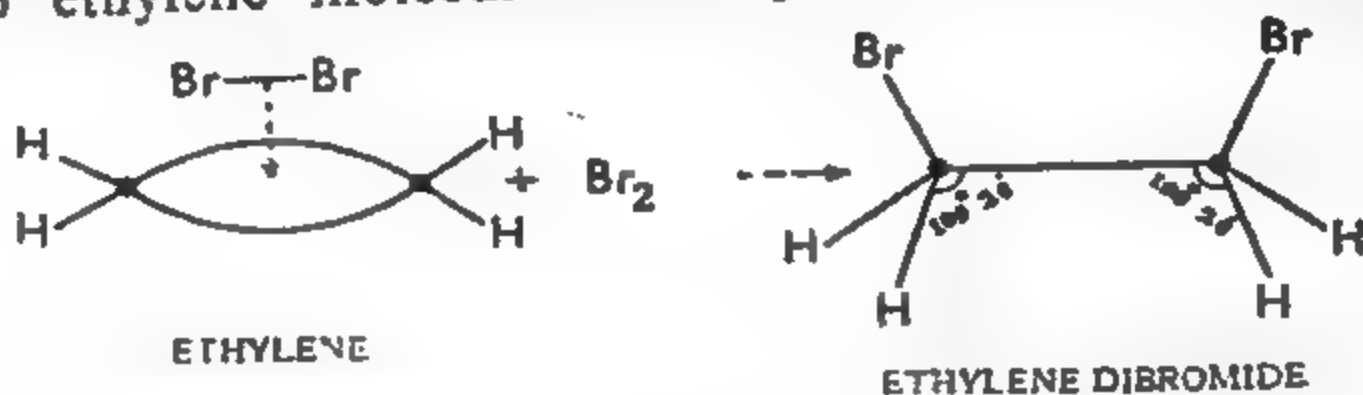


Fig. 5. Mechanism of addition to a double Bond

formation of a saturated compound in which the valencies are directed at normal angles. The molecule now is free of strain and, therefore, more stable.

According to the modern concept, a double bond actually comprises of two kinds of bonds of markedly different strengths; the stronger one is called a *sigma* (σ) *bond* and the weaker one, a *pi* (π) *bond*. The reactivity of the double bond is due to the weak π bond which is far easier to be ruptured.

Resonance. Another concept which has lately played a significant role in explaining the structure of a large number of organic compounds is resonance. If two or more than two different structures can be written for a certain compound and these structures differ from one another only in respect of distribution of electrons, their atomic nuclei remaining in identical positions, then the actual structure of the compound is said to be the 'resonance hybrid' of all these structures. For example, in case of benzene, C_6H_6 , the actual structure is supposed to be a 'resonance hybrid' of the Kekule's structures. (A double headed arrow is used to indicate resonance),



Various structures must have almost similar energy.

Another well-known example is that of a carboxylate ion, which is represented as



It is to be fully understood that the true character of the compound is not represented by any one of the resonating forms. Quite often, a biological analogy, a horse-mule-donkey is given. Here mule is a resonance hybrid of horse and donkey (Whelan D). But this analogy need not be taken too far.

QUESTIONS

1. Explain clearly the cause of chemical combination of the atoms. How would you distinguish between electrovalency, covalency, and co-ordinate valency? Give examples. What type of valency is concerned chiefly in organic compounds?
2. Explain the formation of the following compounds on the basis of electronic theory of valency:

(i) Methane (ii) Ethane (iii) Carbon tetrachloride (iv) Ethylene (v) Ethylene dichloride (vi) Cyclo-propane.

3. What is meant by structural formula ? What is its importance in organic chemistry ? Give the structural formula of (i) Propane (ii) Ethyl alcohol (iii) Dimethyl ether (iv) Acetone and (v) Acetic acid.

4. Write a full account of isomerism of organic compounds.

5. Differentiate clearly between (i) Chain Isomerism (ii) Position isomerism (iii) Functional isomerism and (iv) Tautomerism Give examples.

6. Explain the terms (a) Single bond (b) Double bond (c) Triple bond. How do they differ in their chemical reactivity ?

7. Show how the following compounds are isomers of one another (a) propylene and cyclo propane (b) normal butane and isobutane (c) diethyl ether and methyl propyl ether (d) normal propyl alcohol and iso-propyl alcohol (e) dimethyl ether and ethyl alcohol.

8. Write notes on : Single bond, Double bond and Triple bond. How is it that a single bond is strongest of all ?

9. What is meant by covalent and electrovalent linkages. Which of these linkages occur in organic compounds ? Give the electronic formula of methane.

(Panjab Inter. 1963)

10. (a) Explain the terms 'electrovalency' and 'covalency'.

(b) Discuss the following statement :

"The existence of organic compounds is consequent on the tendency of carbon atoms to form covalent linkages with one another and with atoms of other elements". Illustrate your answer by referring to simple organic substances.

11. Give the electronic concept of the cause of chemical combination. What kind of linkage is usually obtained in *organic* compounds ? How does it differ from that in inorganic compounds ? Exemplify your answer with special reference to the behaviour of sodium chloride and carbon tetrachloride.

(Panjab Inter. 1952)

12. What do you understand by the expression "Tetra Covalency of Carbon" ? Explain the significance of the "single bond", "double bond", and a "triple bond". Arrange them in the order of their strengths giving reasons for your answer. Give at least one example of the substances containing (i) single bond only (ii) at least one double bond (iii) at least one triple bond.

13. Define (a) Molecular formula (b) Structural formula and (c) Electronic formula of a substance bringing out clearly the difference between the three.

Write down the electronic formulae of ethane, acetylene, acetaldehyde, formic acid.

(Panjab Inter. 1955)

14. Fill in the blanks :

(i) Isomerism is the phenomenon.....

(ii) Structural isomerism

(iii) Stereoisomerism is of... types (a) ... and (b) ...

(iv) Electrovalent linkage is caused by.... of electrons from one atom to

(v) Covalent bond involves ... of electrons between two ...

(vi) A double bond is a sign of It is indicated by reactions.

(vii) Ethyl alcohol and dimethyl ethers are examples showing type of structural isomerism.

(viii) A carbon atom is assumed to be situated at the.... of a regular and its four ... are directed towards four

(ix) A triple bond is weaker than ... which in turn is weaker than ... bond

(x) A single covalent bond involves a sharing of one... of electrons and a double bond involves a ... of two ... of electrons.

(xi) A type of linkage wherein the pair of electron is contributed by only one of the atoms is called a bond.

15. Explain :

(1) Tetra valency of the carbon atom.

(2) Significance of single, double and triple bonds.

Illustrate your answer by taking examples from saturated and unsaturated hydrocarbons.

(Panjab T. D.C., Part I, 1963 S)

CHAPTER XXIV

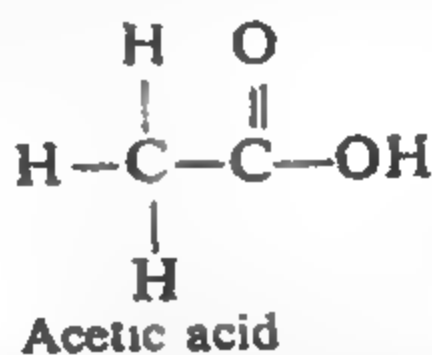
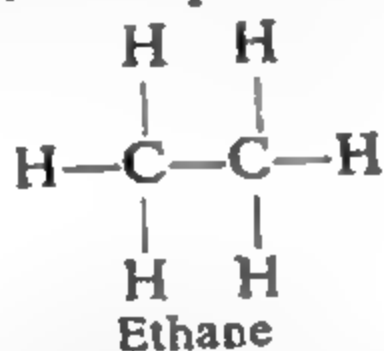
CLASSIFICATION AND NOMENCLATURE OF ORGANIC COMPOUNDS

As already mentioned, the number of organic compounds is usually large. It is essential, therefore, to divide and subdivide them into different types and classes so as to systematise the study of the subject. Fortunately it has been possible to do so.

Broadly speaking, there are two main types of compounds.

(a) **Open (or straight) Chain Compounds.** These are also known as **aliphatic compounds**. The name is derived from the word 'fat' because the earlier compounds of this type were discovered in fats.

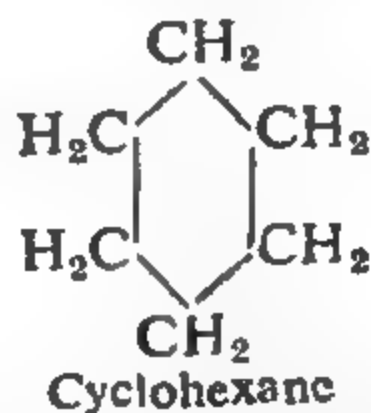
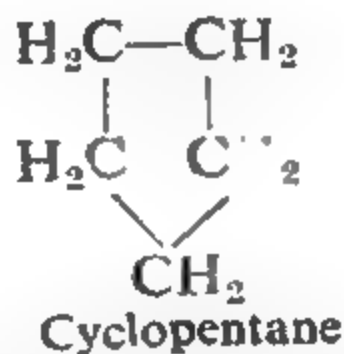
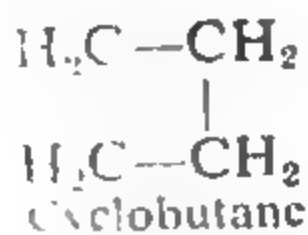
In these substances, the carbon atoms are linked together in open chains, as for example, in ethane and acetic acid.



(b) **Close Chain or Cyclic Compounds.** These compounds contain at least one ring and are, therefore, also known as **ring compounds**.

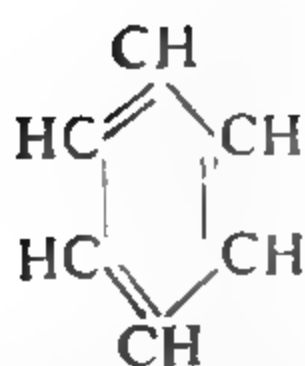
The cyclic compounds are of three main kinds ;

(i) **Alicyclic Compounds.** These substances are *carbocyclic ring compounds*, that is, the ring in these compounds consists of *carbon atoms only*. However, there is no double bond in the ring in such compounds. The examples, are cyclobutane, cyclopentane, cyclohexane, etc., as shown below :

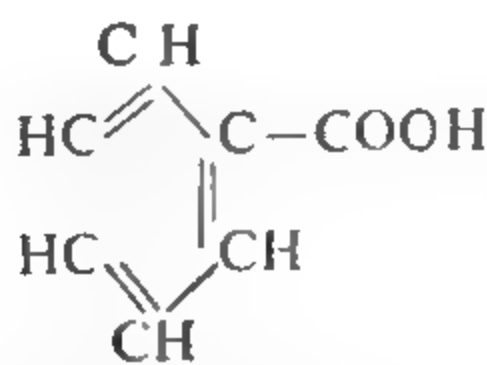


(ii) **Aromatic Compounds.** These substances are also carbocyclic ring compounds but they differ from them in having at least one benzene ring that is, a ring with *alternate double and single bonds*. For example,

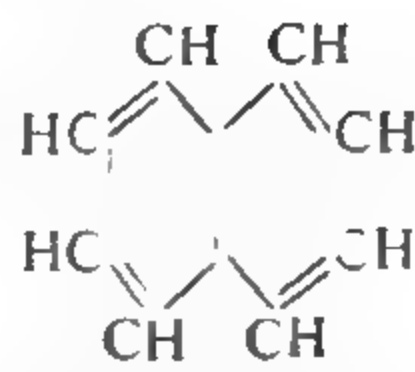
CLASSIFICATION AND NOMENCLATURE



Benzene

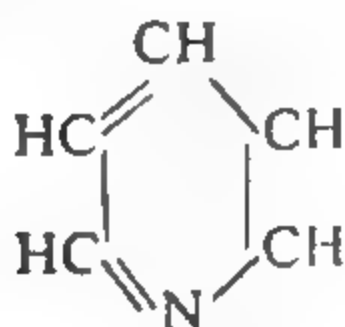


Benzoic acid

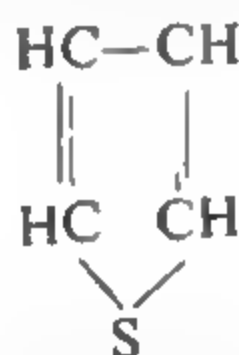


Naphthalene

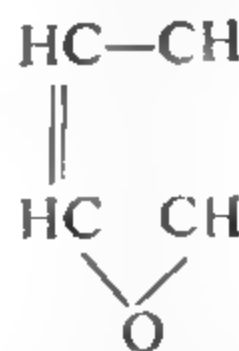
(iii) **Heterocyclic Compounds.** These compounds contain other elements such as sulphur, oxygen, nitrogen, besides carbon, in the ring. For example,



Pyridine



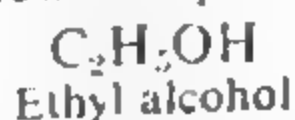
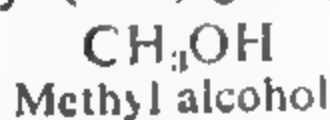
Thiophene



Furan

Homologous Series. Organic compounds can be divided into different series, each series containing a number of closely related substances. Such series are said to be **homologous series** and their individual members are called **homologues**. Consider simple hydrocarbons of *alkane series* viz., CH_4 (methane), C_2H_6 (ethane), C_3H_8 (propane), C_4H_{10} (butane), C_5H_{12} (pentane). Each member differs from the preceding member in composition by $-\text{CH}_2-$. We may also regard each succeeding member to be derived from the preceding one by replacement of one hydrogen atom by a $-\text{CH}_3$ group. It is also evident that all members of the same series have the same general formula. Thus the general formula of the alkane series is $\text{C}_n\text{H}_{2n+2}$ where n is the number of carbon atoms.

If a hydrogen atom in the above compounds is replaced by a hydroxyl (OH) group, the new compounds will be



Now in this new series also, each member differs from the next by CH_2 . Further the same general formula, $\text{C}_n\text{H}_{2n+1}\text{OH}$ represents the composition of every member.

Similarly there are other homologous series such as aldehydes, ketones, fatty acids, amines, etc.

Characteristics of Homologous Series. The compounds belonging to the same homologous series have the following characteristics.

1. They have the same general formula, as shown above.
2. They show similar chemical reactions.
3. They can be prepared by the same general methods.
4. Their physical properties such as solubility, density, melting point, boiling point, etc., show a gradual change with increase in molecular weight of the compounds.
5. The first member of each series sometimes shows an unusual behaviour.

These facts have simplified the subject a great deal.

Functional Groups. All members belonging to any one homologous series contain one *specific group* which largely determines their properties. Such groups are, therefore, **functional groups**. The presence of *the same functional group* in all members of a homologous series accounts for the similar properties of the members of that series. If the properties of one representative member are known, the properties of other members of the same series can usually be predicted. All aldehydes, for example, contain the—CHO group as the functional group. *The properties of all aldehydes are, therefore, really the properties of this group.* The same is true of alcohols, ketones, amines, acids, etc.

The number of functional groups in organic chemistry is much smaller than the total number of compounds. *Therefore, by putting emphasis on the functional group present in each homologous series, it has been possible to systematise and simplify the study of organic chemistry.*

Nomenclature of Organic Compounds

By nomenclature is meant a suitable system of naming compounds so that they may be correctly understood by chemists all over the world.

In early days, a number of organic compounds were named on the basis of their origin, for example, urea and uric acid (from urine); malic acid (from apple; *malum* in Latin means apple); methyl alcohol (from wood distillation; *methu* meaning wine and *hule* meaning wood in Greek), etc. This system of naming organic compounds is known as **common or trivial system**.

The trivial system had the advantage that the names were simple and could be easily remembered. But with ever growing number of organic compounds, the need was felt to evolve a new system which may indicate the *structure* of the compounds rather than the source from which it was obtained. Accordingly an International Commission was called in 1895 at Geneva to decide upon a system of nomenclature which is known as the **Geneva system of nomenclature**. The work was further carried on by a committee known as the **International Union of Chemists (I.U.C.)**. After nine years of labour they drew up in 1931, a scheme which is now referred to as the **I.U.C. system**.

The nomenclature of a few important homologous series is given below :

(1) **Alkanes or Paraffins.** The alkanes are the most important amongst other parent substances because a number of compounds belonging to the families can be considered to have been derived from them. The first four members of the paraffin series have special names derived from history. The fifth and higher members are named according to the number of carbon atoms contained in the molecule. Thus we have

CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane

C_5H_{12}	Pentane
C_6H_{14}	Hexane
C_7H_{16}	Heptane
C_8H_{18}	Octane

and so on.

The general formula of alkanes is C_nH_{2n+2} .

(2) **Alkenes or Olefins.** Alkenes or olefins are the unsaturated hydrocarbons containing one double bond. Their general formula is C_nH_{2n} . The names of the individual members are derived from alkanes containing the same number of carbon atoms, by changing the suffix *—ane* to *—ene*. Thus we have

<i>Formula</i>	<i>I.U.C. name</i>	<i>Common name</i>
CH_2	Methene	Methylene
C_2H_4	Ethene	Ethylene
C_3H_6	Propene	Propylene
C_4H_8	Butene	Butylene
C_5H_{10}	Pentene	Amylene

(3) **Alkynes or Acetylenes.** Alkynes or acetylenes have the general formula C_nH_{2n-2} . They contain one triple bond. The name of each member is derived from the corresponding alkane by replacing the suffix *—ane* by *—yne*. The names of first four members of the series are given below :

<i>Formula</i>	<i>I.U.C. Name</i>	<i>Common Name</i>
C_2H_2	Ethyne	Acetylene
C_3H_4	Propyne	Allylene
C_4H_6	Butyne	Crotonylene
C_5H_8	Pentyne	

(4) **Alkyl Radicals.** Alkyl radical is of great importance in organic nomenclature. It is derived from an alkane by the removal of one hydrogen atom. The radical is named after the corresponding alkane by changing the suffix from *—ane* to *—yl*. The first four alkyl radicals are given below :

<i>Formula of radical</i>	<i>Alkane from which derived</i>	<i>Name of the alkyl radical</i>
CH_3-	CH_4 , Methane	Methyl
C_2H_5-	C_2H_6 , Ethane	Ethyl
C_3H_7-	C_3H_8 , Propane	Propyl
C_4H_9-	C_4H_{10} , Butane	Butyl

Sometimes the alkyl radical in compounds is represented merely by the letter R. This is the usual practice where the main emphasis is on the other group or groups which are present in the molecule. Thus when the properties of halogen derivatives of alkanes are under study where the halogen group and not the alkyl group is taking any significant part, the compounds are written as $R-Cl$ or $R-Br$ as the case may be. R represents any alkyl radical (methyl, ethyl, etc.) that may be present in the molecule.

(5) **Alcohols.** According to the new system of nomenclature, alcohols are named after the alkanes from which they may be considered to be derived by replacing the last letter 'e' by the syllable 'ol' as shown below:

Formula	Alkane from which derived	I. U. C. name	Common name
CH_3OH	CH_4 , Methane	Methanol	Methyl alcohol
$\text{C}_2\text{H}_5\text{OH}$	C_2H_6 , Ethane	Ethanol	Ethyl alcohol
$\text{C}_3\text{H}_7\text{OH}$	C_3H_8 , Propane	Propanol	Propyl alcohol
$\text{C}_4\text{H}_9\text{OH}$	C_4H_{10} , Butane	Butanol	Butyl alcohol

Thus all alcohols end in 'ol' and as a class they are called **alkanols**, the general formula being $\text{C}_n\text{H}_{2n+1}\text{OH}$.

Sometimes an alcohol may contain two or more hydroxyl groups. In such cases, they are classified as *dihydric*, *trihydric* or *polyhydric* alcohols according to the number of hydroxyl groups contained. For example,

Formula	I.U.C. name	Common name
CH_2OH CH_2OH	Ethanediol	Ethylene glycol or glycol
CH_2OH CHOH CH_2OH	1,2,3, Propanetriol	Glycerol

(6) **Ethers.** Ethers may be regarded as derived from alkanes by replacing two hydrogen atoms (one from each molecule) by one oxygen atom. Their general formula is represented as $\text{R}-\text{O}-\text{R}$ or $\text{R}-\text{O}-\text{R}'$ depending upon the fact whether the two alkyl radicals are the same or different. They are named after the two alkyl radicals contained in them as shown below :

Formula	I.U.C. name	Common name
CH_3OCH_3	Methoxy methane	Methyl ether
$\text{CH}_3\text{O.C}_2\text{H}_5$	Methoxy ethane	Methyl ethyl ether
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Ethoxy ethane	Diethyl ether

(7) **Aldehydes** Aldehydes are named after the alkanes from which they may be considered to be derived by replacing the last letter 'e' by 'al' as shown below :

Formula	Alkane from which derived	I. U. C. name	Common name
HCHO	Methane	Methanal	Formaldehyde
CH_3CHO	Ethane	Ethanal	Acetaldehyde
$\text{C}_2\text{H}_5\text{CHO}$	Propane	Propanal	Propionaldehyde
$\text{C}_3\text{H}_7\text{CHO}$	Butane	Butanal	Butyraldehyde

Thus all aldehydes end in 'al' and as a class they are named as **alkanals**.

(8) **Ketones.** The names of the ketones are derived from alkanes by replacing the last letter 'e' by 'one'. A few examples are given below :

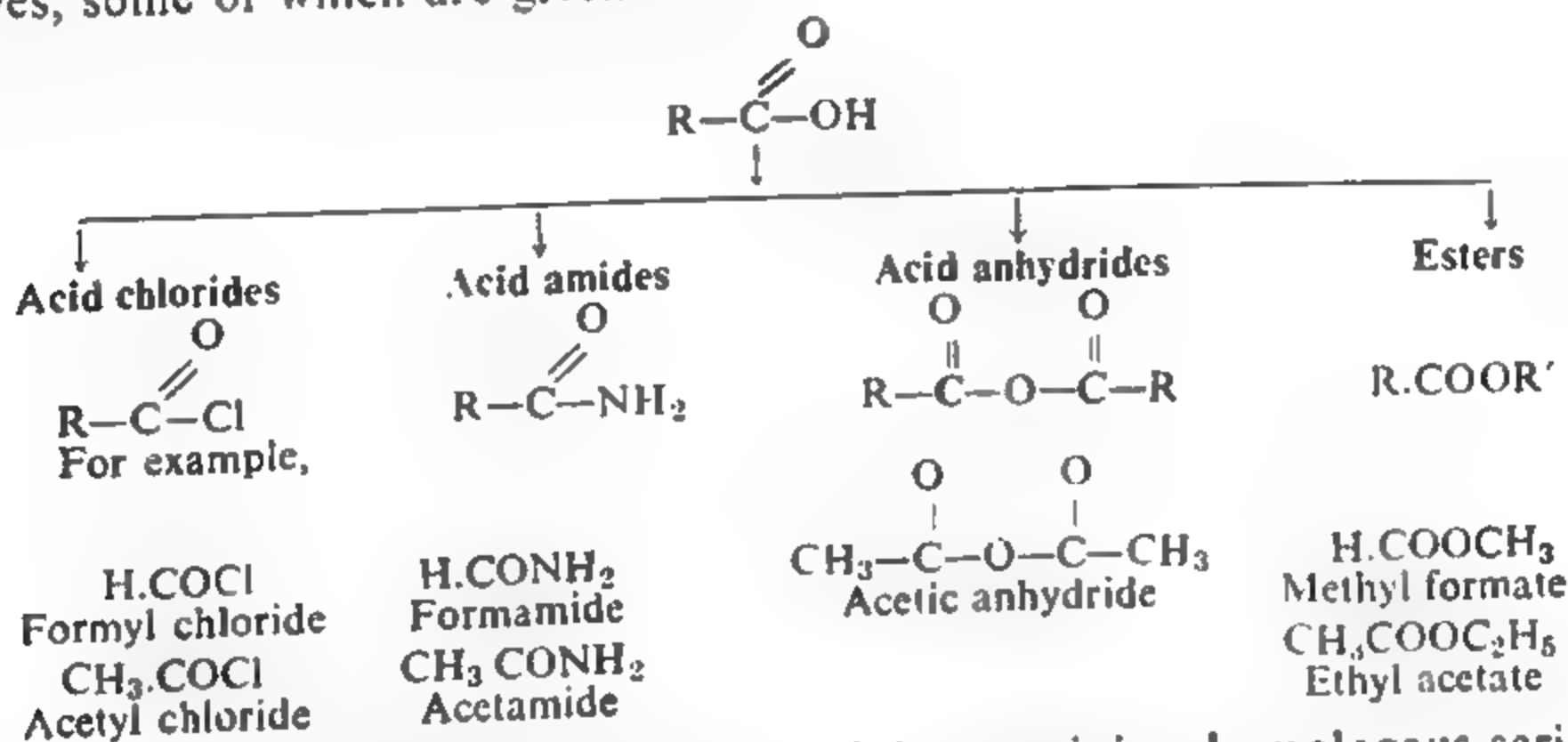
Formula	I. U. C. name	Common name
CH_3COCH_3	Propanone	Dimethyl ketone
$\text{CH}_3\text{CO.C}_2\text{H}_5$	Butanone	Methyl ethyl ketone
$\text{C}_2\text{H}_5\text{CO.C}_2\text{H}_5$	Pentanone	Diethyl ketone
$\text{C}_2\text{H}_5\text{CO.C}_3\text{H}_7$	Hexanone	Ethyl propyl ketone

Thus, all ketones end in 'one' and are called **alkanones**.

(9) **Fatty Acids.** The fatty acids, on analogy with the above classes of compounds, are called **alkanoic acids**. A few examples are given below :

<i>Molecular formula of the acid.</i>	<i>I. U. C. name</i>	<i>Common name</i>
H COOH	Methanoic acid	Formic acid
CH ₃ COOH	Ethanoic acid	Acetic acid
C ₂ H ₅ COOH	Propanoic acid	Propionic acid
C ₃ H ₇ .COOH	Butanoic acid	Butyric acid

(10) **Derivatives of Fatty Acids** Fatty acids give a number of derivatives, some of which are given below :



(11) **Other Organic Series.** Some of the remaining homologous series their general formulae, the functional groups contained in them and the name of two simplest members of each series are given below :

Name of series	Functional group	General formula	Two simple members of the series
Amines	-NH ₂	R-NH ₂ or C _n H _{2n+1} .NH ₂	CH ₃ NH ₂ Methyl amine C ₂ H ₅ NH ₂ Ethyl amine
Nitroparaffins	$-\text{N} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array}$	R.NO ₂ or C _n H _{2n+1} .NO ₂	CH ₃ NO ₂ Nitromethane C ₂ H ₅ NO ₂ Nitroethane
Alkyl nitrites	-O-N=O	R-O-N-O or C _n H _{2n+1} -O-N-O	CH ₃ -O-N=O Methyl nitrite C ₂ H ₅ -O-N=O Ethyl nitrite

Continued

Continued :

Nitriles (cyanides)	$-\text{C}\equiv\text{N}$	R.CN or $\text{C}_n\text{H}_{2n+1}.\text{CN}$	CH_3CN Methyl cyanide $\text{C}_2\text{H}_5\text{CN}$ Ethyl cyanide
Grignard reagents	$-\text{MgX}$ (where X may be any halogen)	R.MgX or $\text{C}_n\text{H}_{2n+1}.\text{MgX}$	CH_3MgI Methyl magnes- ium iodide $\text{C}_2\text{H}_5\text{MgI}$ Ethyl magnesium iodide

QUESTIONS

- Discuss the classification of organic compounds. Give examples.
- Explain what you understand by (a) open chain (b) closed chain (c) carboxylic and (d) heterocyclic compounds. To which class do aromatic compounds belong? Why are they called aromatic?
- What is meant by 'nomenclature of organic compounds'? Give the nomenclature for the first three members of paraffins, olefins, alcohols, aldehydes, ketones and acids.
- Explain what you understand by homologous series. Give examples.
- What is a functional group? Discuss its importance in organic chemistry.
- What is alkyl radical? Write formula of four different alkyl radicals each associated with a different functional group. Name the compound in each case.
- Give the general formula and functional group of each of the following series of compounds :
 - Alcohols
 - Aldehydes
 - Ketones
 - Fatty acids
 - Ethers
 - Amines.
- Write the common and I. U. C. names (where possible) for the following compounds :

(i) CH_3CHO	(ii) CH_3CN	(iii) $\text{C}_2\text{H}_5\text{COCH}_3$
(iv) CH_3COCl	(v) $\text{CH}_3\text{COOC}_2\text{H}_5$	(vi) $\text{C}_2\text{H}_5\text{COOCH}_3$
(vii) HCONH_2	(viii) $\begin{array}{c} \text{CH}_3\text{CO} \diagup \text{O} \\ \text{CH}_3\text{CO} \diagdown \end{array}$	(ix) $\begin{array}{c} \text{CH}_3 \diagup \text{NH} \\ \text{CH}_3 \diagdown \end{array}$
(x) $\text{CH}_3.\text{CHOH}.\text{CH}_3$	(xi) $(\text{CH}_3)_3\text{N}$	
- Write the formulae of the following substances : Formaldehyde, Acetamide, Acetic anhydride, Formyl chloride, Nitroethane, Acetonitrile, Propanone, Methanol, Ethanal, Methanoic acid.

CHAPTER XXV

SATURATED HYDROCARBONS (ALKANES OR PARAFFINS)

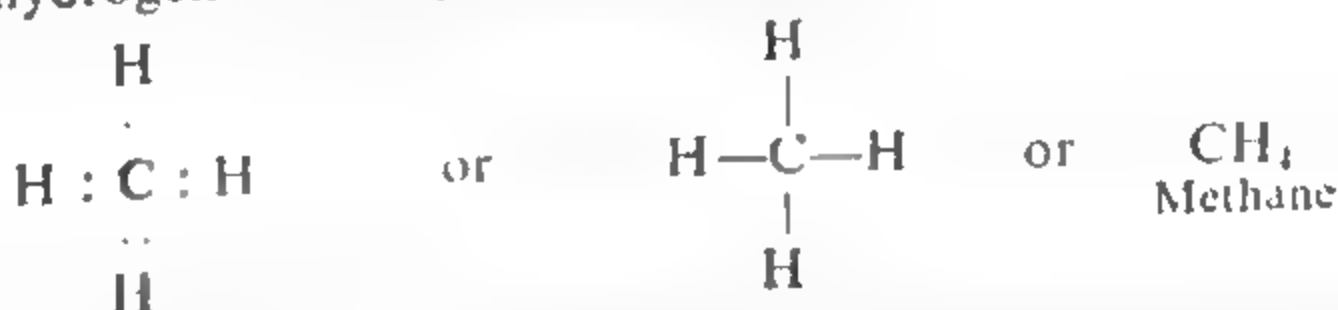
Carbon forms a large number of compounds with hydrogen which are known as **hydrocarbons**. They are divided into two groups :

- (i) *Saturated Hydrocarbons* (ii) *Unsaturated hydrocarbons*

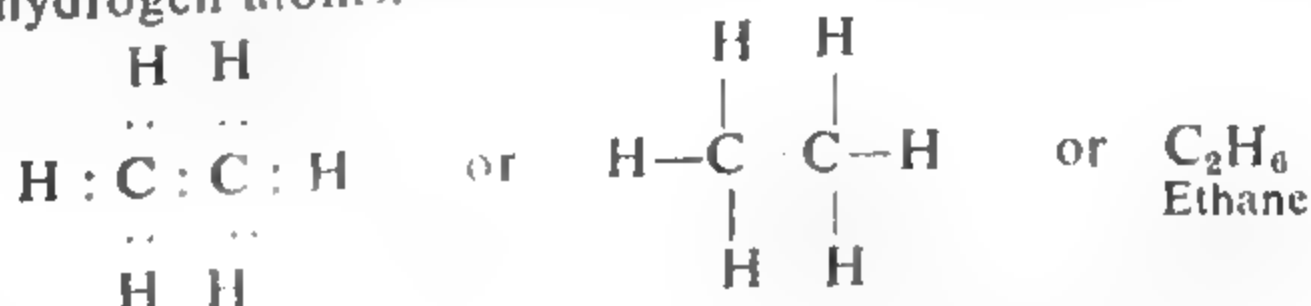
Saturated Hydrocarbons.

Saturated hydrocarbons are those in which all the valencies of carbon atoms are fully satisfied by hydrogen atoms. These compounds are *ordinarily* resistant towards chemical reagents like sulphuric acid, nitric acid, sodium hydroxide, potassium permanganate, potassium dichromate, etc. On account of their very little chemical affinity, they are commonly known as **paraffins** (Latin : *parum*, little ; *affinis*, affinity). They are, however, easily attacked by halogens when the hydrogen atoms are successively replaced by halogen atoms.

The simplest paraffin is methane, consisting of one carbon atom joined to four hydrogen atoms by covalent linkages.



Higher members of the series consist of two or more carbon atoms linked together in chains by covalent bonds. The remaining free valencies are occupied by hydrogen atoms.



The above four hydrocarbons have special names related to their history and from the fifth member onwards, Latin or Greek numerals are used to indicate the number of carbon atoms in the molecule. Thus we have :

Formula	Name	Formula	Name
CH_4	Methane	C_7H_{16}	Heptane
C_2H_6	Ethane	C_8H_{18}	Octane
C_3H_8	Propane	C_9H_{20}	Nonane
C_4H_{10}	Butane	$\text{C}_{10}\text{H}_{22}$	Decane
C_5H_{12}	Pentane	$\text{C}_{11}\text{H}_{24}$	Undecane
C_6H_{14}	Hexane	$\text{C}_{12}\text{H}_{26}$	Dodecane

and so on.

The homologous series formed by the saturated hydrocarbons is represented by the general formula $\text{C}_n\text{H}_{2n+2}$. The hydrocarbons may be of **straight chain** or **branched chain** type. The hydrocarbons with straight chains are termed **normal** (or *n*-) hydrocarbons. Thus

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$ is *n*-butane, and

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ is *n*-pentane.

The hydrocarbons with branched chains are called **iso**-(or **secondary**) and **neo**-(or **tertiary**) depending upon whether there are two or three branched chains attached to the same carbon atom

Thus $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \\ \diagup \\ \text{CH}_3 \end{array} \cdot \text{CH}_3$ is *isobutane*

and $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_3 \end{array} \cdot \text{CH}_3$ is *neopentane*.

The I.U.C. system, which is used for naming higher alkanes, consists in selecting the longest chain of carbon atoms in the molecule and numbering them in such a way that the *carbon atoms carrying the chains have the least possible numbers*, e.g.,

$\begin{array}{cccccc} 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & \text{CH}_2 & \text{CH}_2 & \text{CH} & \text{CH}_3 \\ & & & | \\ & & & \text{CH}_3 \end{array}$ is 2-methyl pentane

and $\begin{array}{cccccc} 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & \text{CH}_2 & \text{CH} & \text{CH} & \text{CH}_3 \\ & & | & | \\ & & \text{C}_2\text{H}_5 & \text{CH}_3 \end{array}$ is 1-methyl, 3-ethyl pentane.

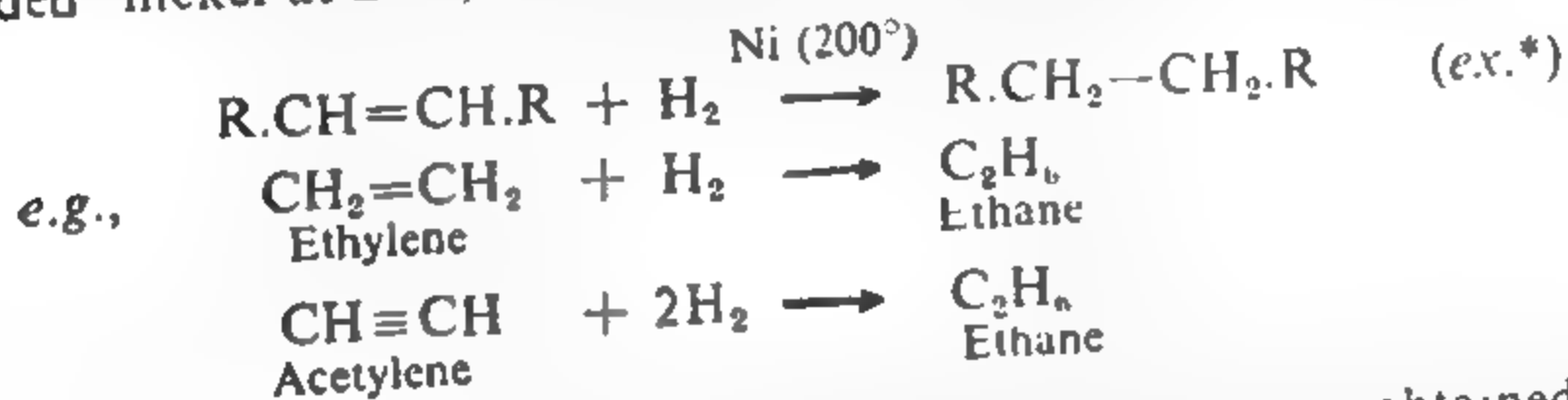
It may be emphasised that in I.U.C. system, *iso*- and *neo*-prefixes are not used.

Occurrence. The paraffins occur in large quantities, in nature. *Marsh gas* issuing out from marshy places consists mainly of methane. *Natural gas* and the gases from oil wells in petroleum regions are mixtures of lower paraffins, mainly methane and ethane. Crude petroleum or mineral

oil provides an unlimited source of liquid hydrocarbons while natural wax found in huge deposits in petroleum areas and elsewhere is nothing but a mixture of solid hydrocarbons.

Large amounts of paraffins are obtained by the destructive distillation of fats and brown coal.

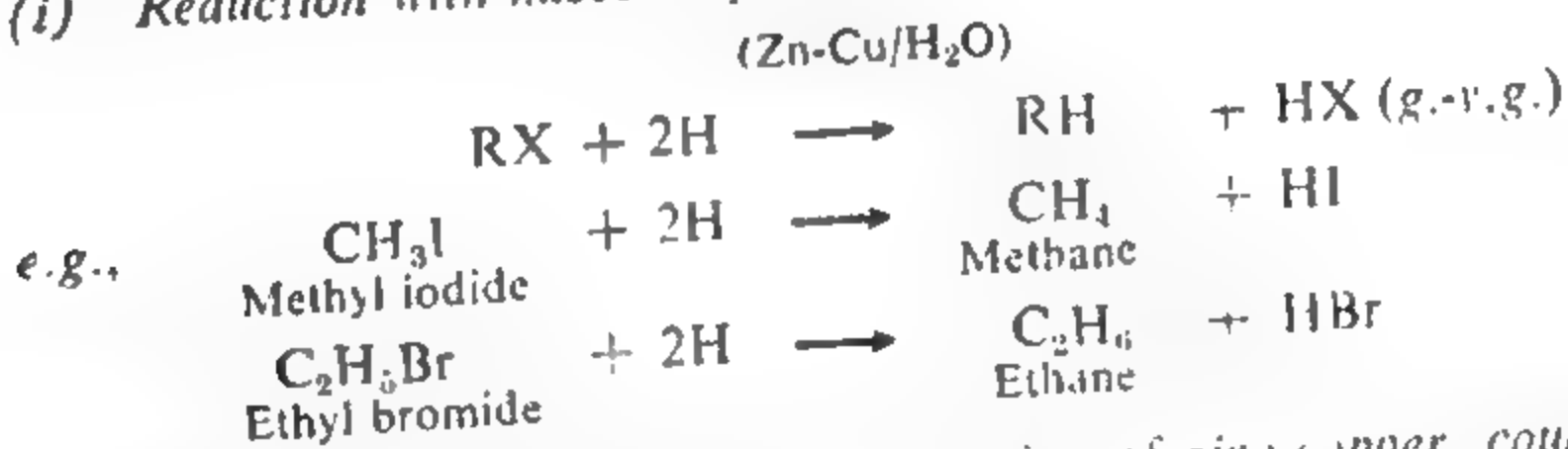
General Methods of Preparation (1) By the catalytic reduction of unsaturated hydrocarbons. (Sabatier Senderen's reaction). When a mixture of unsaturated hydrocarbon and hydrogen is passed over finely divided nickel at 200° , the corresponding paraffin is obtained.



Since large amounts of unsaturated hydrocarbons are obtained as a result of *cracking of petrol*, the above reaction is now used for the *production of paraffins on an industrial scale*.

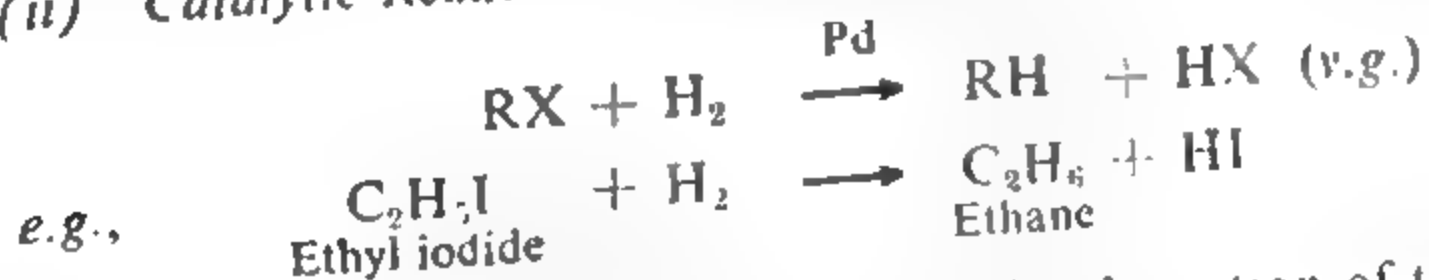
(2) By the reduction of alkyl halides. Alkyl halides may be conveniently converted into the corresponding paraffins by a variety of methods such as :

(i) Reduction with nascent hydrogen.



Nascent hydrogen is obtained by the action of zinc-copper couple on water or alcohol.

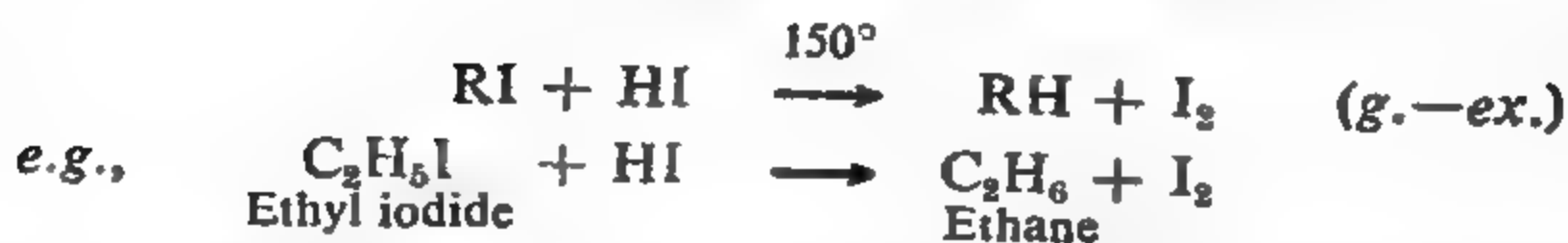
(ii) Catalytic Reduction. Palladium is used as a catalyst.



Hydrogen for this reaction is produced by the action of tin on hydrochloric acid.

(iii) Reduction with concentrated hydriodic acid under pressure. An alkyl halide when heated with concentrated hydriodic acid at 150° , in a sealed tube or in an autoclave gives rise to corresponding paraffins.

*The meaning of these abbreviations are explained in the preface.

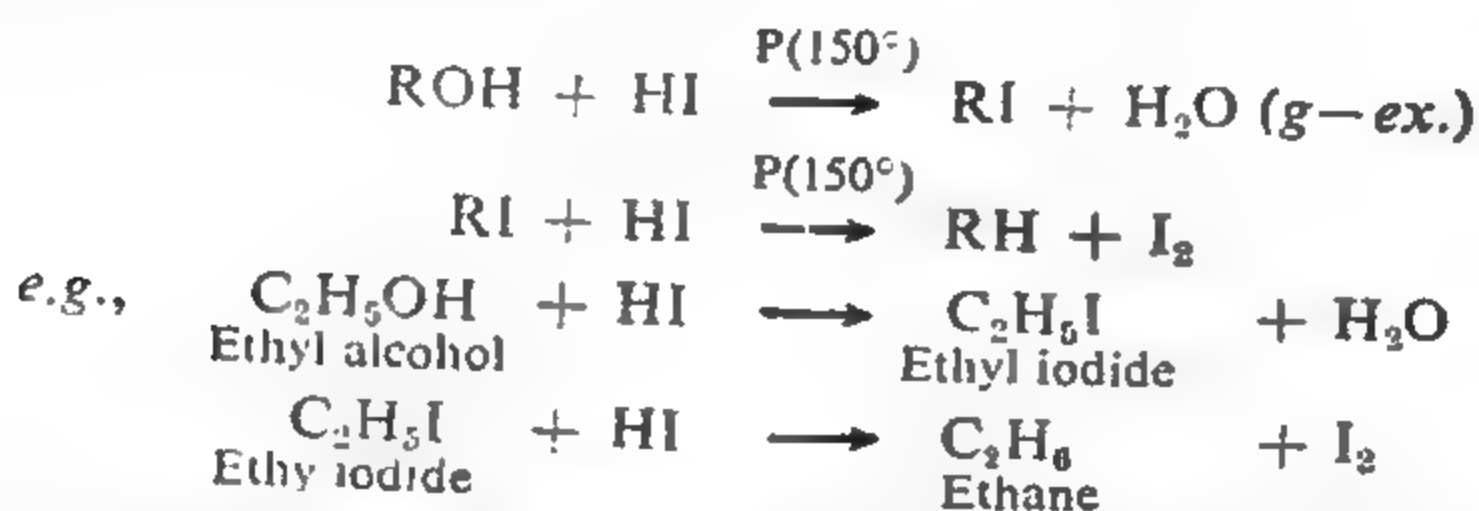


Reduction with HI is usually carried out in the *presence of red phosphorus* which helps in the regeneration of HI from the iodine formed.

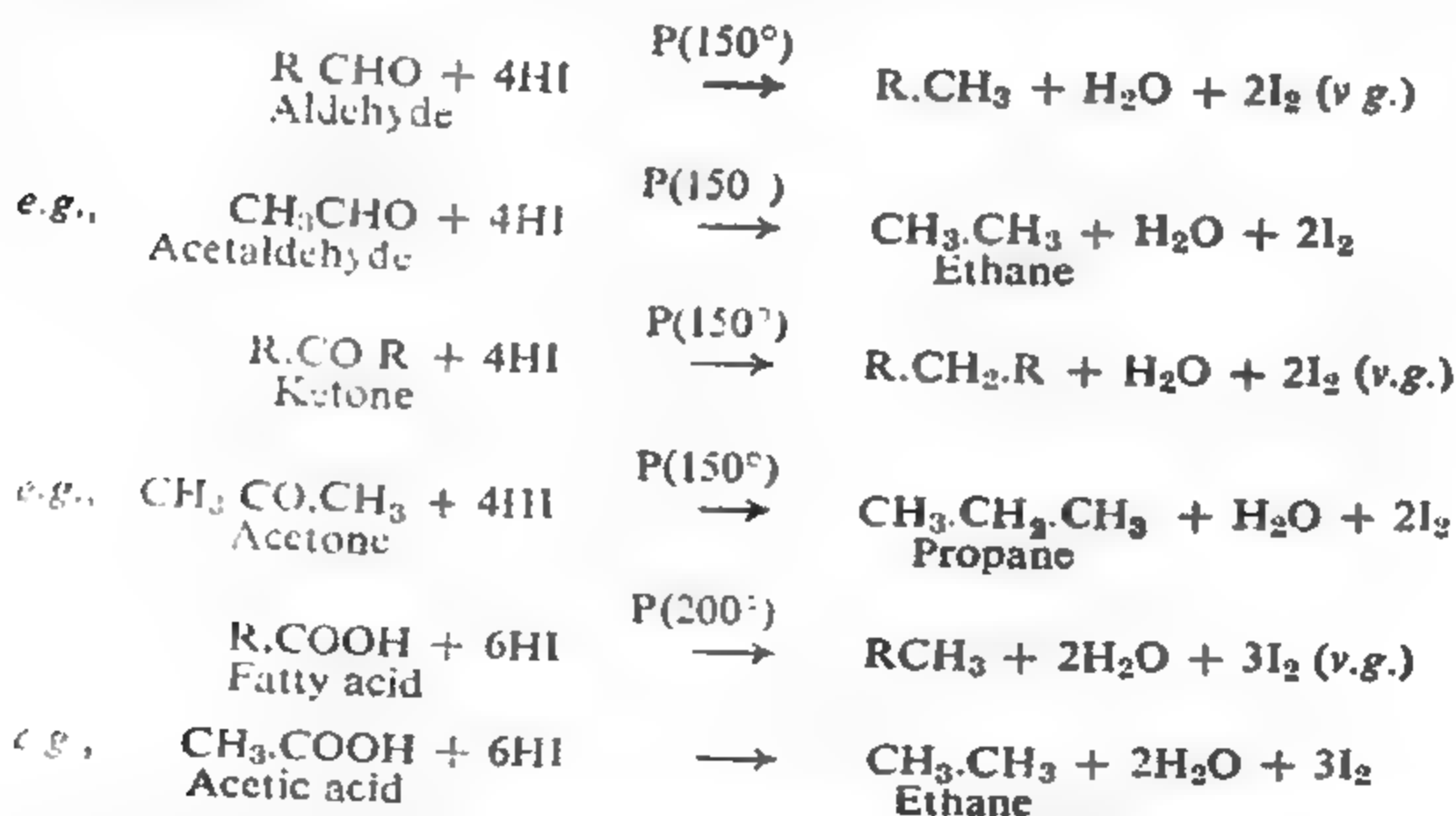


The *hydriodic acid-red phosphorus mixture*, provides one of the most effective reducing agents in organic chemistry.

(3) **By the reduction of alcohols.** Instead of an alkyl halide, an alcohol can also be taken and reduced by heating with *hydriodic acid-red phosphorus mixture*. The first step in this reaction is the conversion of alcohol into the alkyl iodide which is then reduced further to give the hydrocarbon.

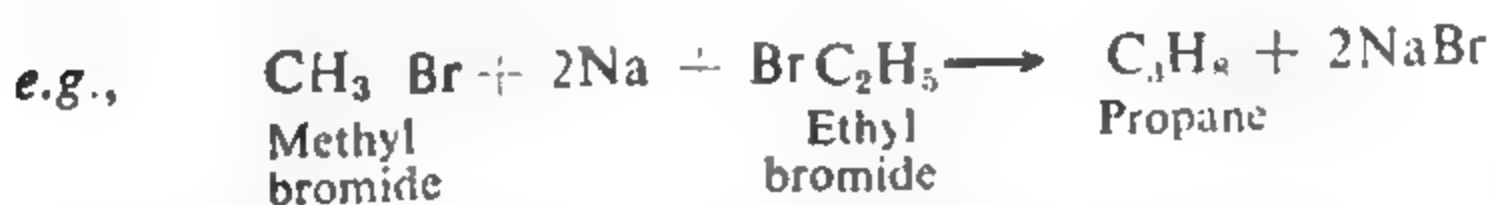
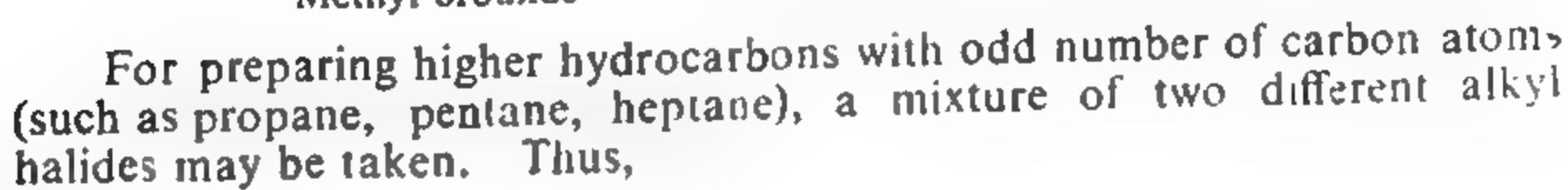


(4) **By the reduction of aldehydes, ketones and fatty acid.** Aldehydes, ketones or fatty acids can also be reduced by *hydriodic acid and red phosphorus* to the corresponding paraffins.



This method gives very good yield particularly in case of higher paraffins.

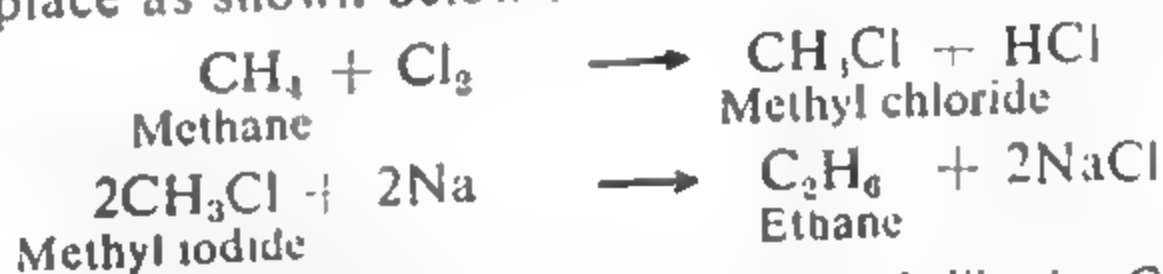
(5) **By the Wurtz reaction.** In this method, an ethereal solution of an alkyl halide (preferably the bromide or the iodide) is treated with

$$R-X + 2Na + X-R \xrightarrow{\text{dry ether}} R-R + 2NaX$$


But in this case, in addition to the desired paraffin RR' , the paraffins $R-R$ and $R'-R'$ are also formed :

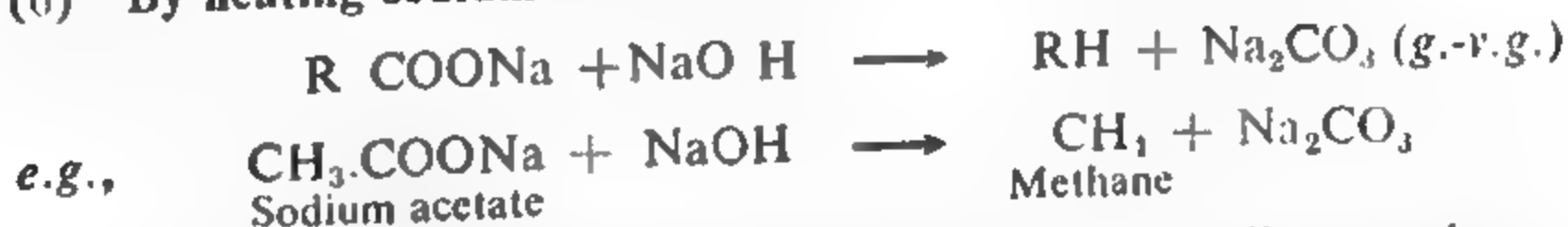


The Wurtz synthesis provides a good method for getting a higher hydrocarbon from a lower one. For example, the conversion of methane into ethane takes place as shown below :



Wurtz reaction has also been carried out using other metals like Ag, Cu, etc. [But Na works best. Further, Wurtz reaction gives best yields in case of preparation of paraffins containing even carbon atoms.

(6) By heating sodium salt of a fatty acid with soda lime*.



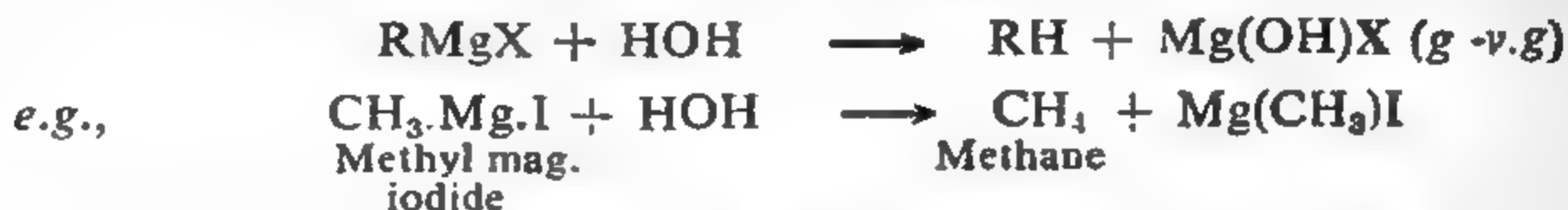
In this case, the carboxyl group of the acid is split off as carbonate. This process of eliminating carbon dioxide from a carboxylic acid is known as **decarboxylation**.

This method works well only in case of sodium acetate. In case of higher members, e.g., propionate, butyrate, etc., a number of products are formed. For instance with sodium propionate, we have (Oakwood 1950)



*Sodalime is a mixture of sodium hydroxide and quicklime (CaO). Sodium hydroxide alone is not used as it is deliquescent and easily fusible.

(7) **From Grignard reagents.** Grignard reagents are easily decomposed by water into the paraffin and a basic magnesium salt.



(8) **By the electrolysis of the alkali salts of fatty acids (Kolbe's electrolytic method).** Moderately concentrated solution of sodium (or potassium) salt of a fatty acid is subjected to electrolysis to yield a paraffin.



At anode : The negative acid radical ions go to the anode where they decompose into carbon dioxide and a paraffin.



At cathode : The H^+ ions (furnished by small ionisation of water) move towards the cathode, and are discharged giving hydrogen.



Thus, sodium acetate on electrolysis gives ethane.



This method is *excellent for preparation of hydrocarbons beyond hexane.*

(Methods numbered 1, 5, 8, are not applicable for the preparation of methane).

General Properties of the Paraffins. (a) **Physical Properties.** The paraffins from C_1 (methane) to C_4 (butane) are colourless, odourless gases, those from C_5 to C_{17} are colourless highly volatile liquids with a 'benzine' odour while the higher members are colourless non-volatile solids. They are practically insoluble in water but are freely soluble in organic solvents like ether, acetone, carbon tetrachloride, etc. Other physical properties such as melting points, boiling points, viscosity and specific gravity increase fairly regularly with increase in the number of carbon atoms.

(b) **Chemical Properties.** As already stated the paraffins are stable compounds and are *apparently unreactive*. In recent years, however, they have been shown to undergo important chemical reactions such as oxidation, nitration, sulphonation, etc., *under suitable conditions*.

The most important reactions of the paraffins are :

(1) **Halogenation.** It is the *process of replacing hydrogen atoms of the hydrocarbon by halogen atoms.*

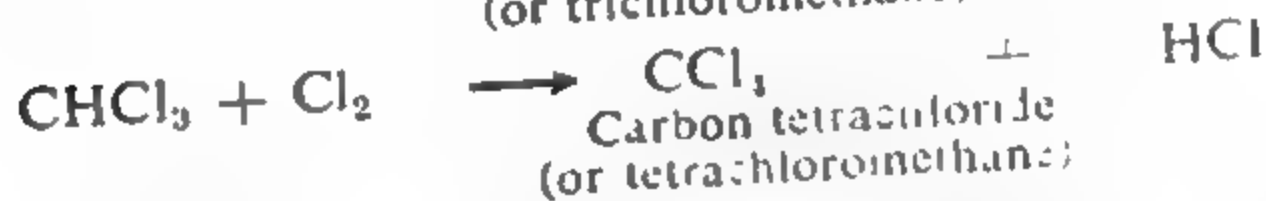
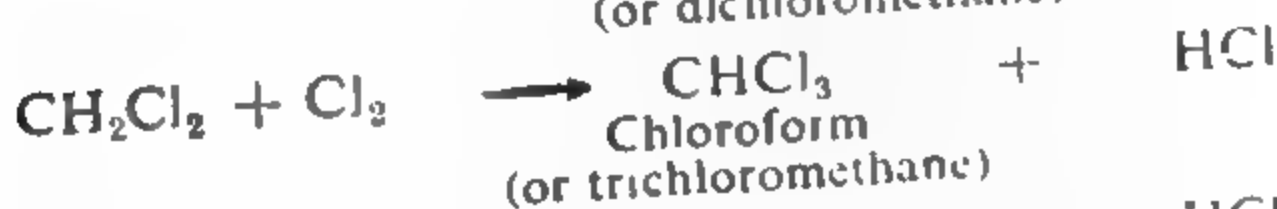
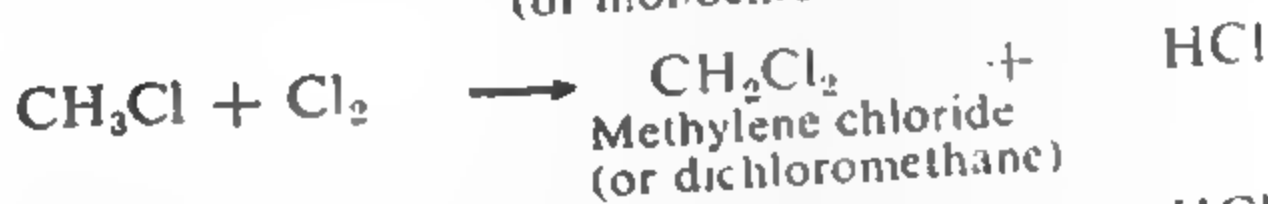
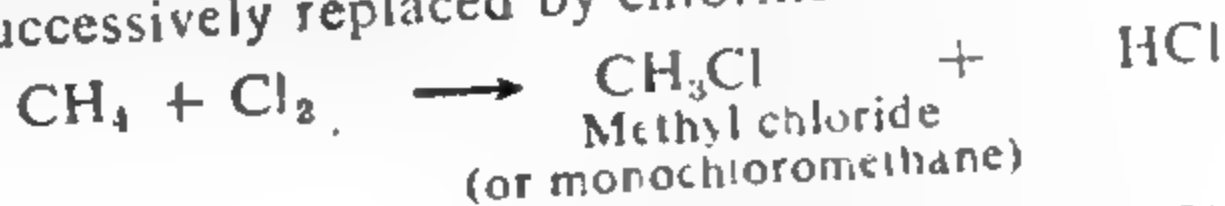
SATURATED HYDROCARBONS

(a) *Chlorination.* Paraffins are not attacked by chlorine in the absence of light.

In *direct sunlight*, the reaction of chlorine with methane is so vigorous that the hydrocarbon decomposes with an explosion giving carbon.



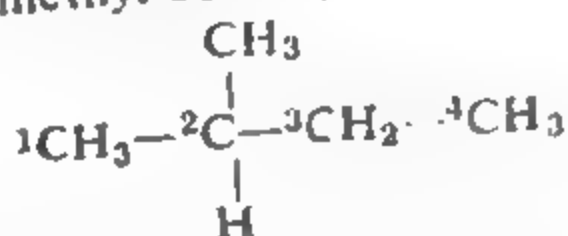
In *diffused sunlight*, however, the reaction is smooth, the hydrogen atoms are successively replaced by chlorine atoms.



This process of the replacement of a hydrogen atom by another atom (or radical) is called **substitution**.

It is interesting to note that all the hydrogen atoms in the hydrocarbon are not equally reactive. Their order of reactivity is tertiary > secondary > primary.*

Thus, in the case of 2-methyl butane,



chlorination takes place successively at the carbon atoms numbered 2, 3 and 4.

(b) *Bromination.* Bromination, though similar to chlorination, is not so vigorous.

(c) *Iodination.* Direct iodination of paraffins has not been successful because the *hydriodic acid* liberated reduces the alkyl iodide back to the original paraffin.



So iodination can be carried out only in the presence of an oxidising agent (such as iodic acid, nitric acid, mercuric oxide, etc.) which converts the HI formed into iodine.



(2) *Nitration.* Lower paraffins are not attacked by nitric acid but higher hydrocarbons from hexane upwards, after a long continued treatment, suffer replacement of a hydrogen atom by a nitro (NO_2) group. This

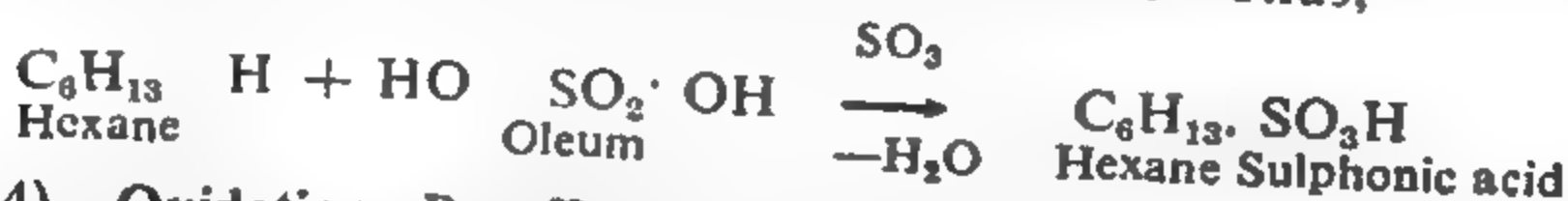
*(For meaning of the terms, primary, secondary and tertiary carbon atoms, see page 271).

process is known as **nitration**. For example, hexane when treated with *fuming nitric acid* for 40 hours is converted into nitrohexane.



Vapour phase nitration. This is the modern method of nitration developed by Hass (1936) and has been successfully employed for the nitration of all hydrocarbons including methane. In this process, a gaseous mixture of the hydrocarbon and nitric acid *vapour* is passed through a narrow tube at about 420° (475° in case of methane) at atmospheric pressure to get the corresponding nitro compound. Of late, nitro hydrocarbons, because of their non-flammability, have found *extensive use as solvents* especially for plastics, rubber, etc.

(3) **Sulphonation.** It is the process of the *replacement of a hydrogen atom by a sulphonic acid ($-\text{SO}_3\text{H}$) group*. Like nitric acid, sulphuric acid has also no action on the lower paraffins. Higher hydrocarbons, from hexane onwards are, however, attacked by *fuming sulphuric acid* (oleum; viz., $\text{H}_2\text{SO}_4 + \text{SO}_3$) giving alkyl sulphonic acids. Thus,



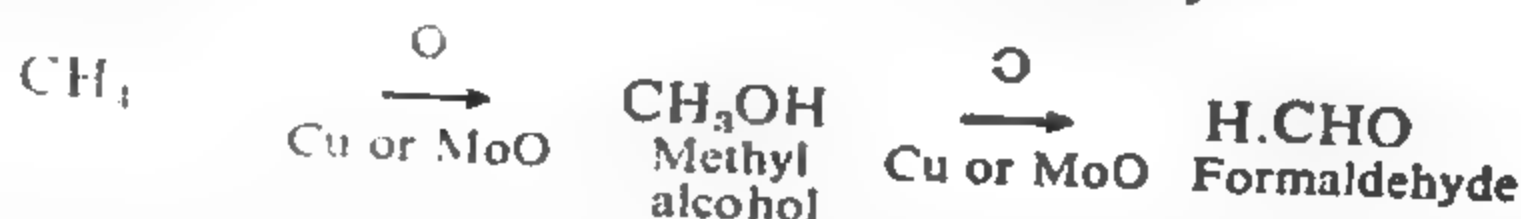
(4) **Oxidation.** Paraffins yield different products on oxidation under different conditions as illustrated below :

(i) **Combustion or complete oxidation.** When burnt in air or oxygen the paraffins are completely oxidised to carbon dioxide and water with the production of a large amount of heat.



(ii) **Incomplete combustion.** Incomplete combustion of gaseous hydrocarbons results in the production of *carbon blacks* which are used in the manufacture of Indian ink, printer's ink, black paints, etc.

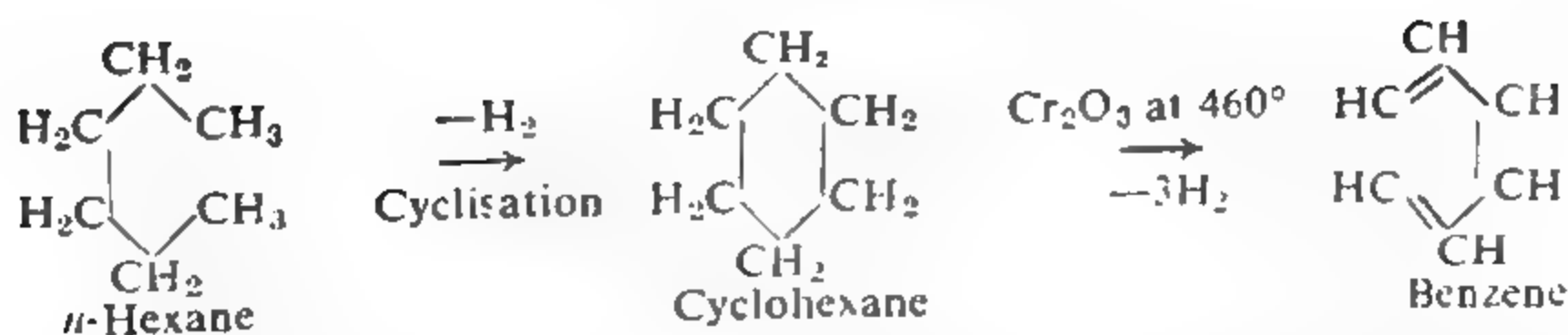
(iii) **Catalytic oxidation.** Partial oxidation of methane by air under high pressure (130—200 atmospheres), in the presence of catalysts (metals and metallic oxides, e.g., Cu, MoO, etc.,) and at high temperatures, results in the production of methyl alcohol and formaldehyde.



Similarly, catalytic oxidation of ethane yields acetaldehyde and acetic acid.

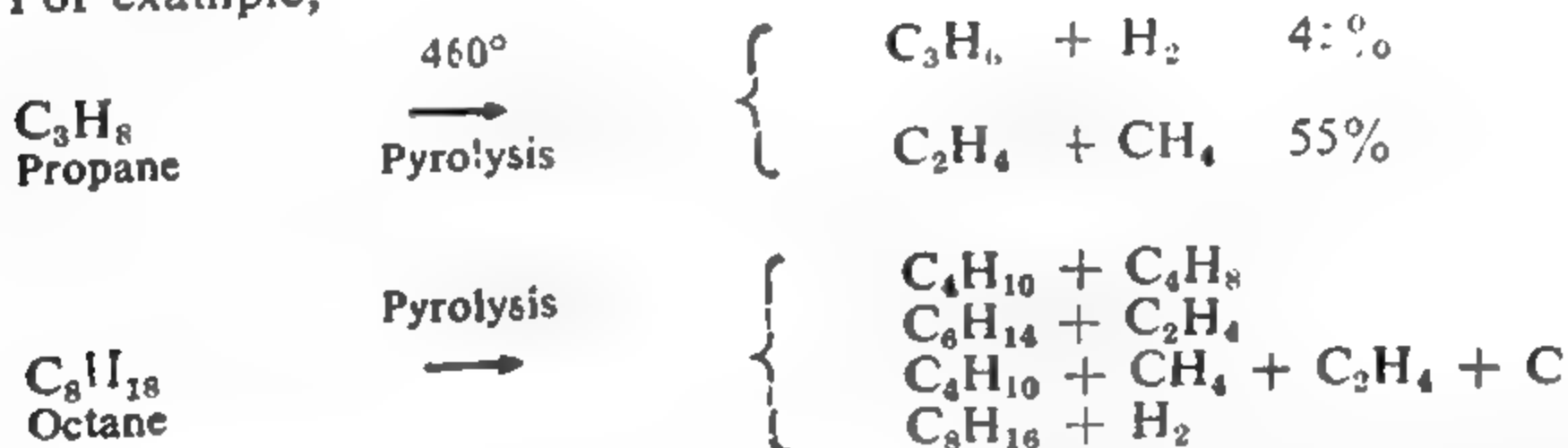
(5) **Aromatisation.** One of the most remarkable achievements of recent years is the production of aromatic hydrocarbons from the paraffins containing six or more carbon atoms, by the action of heat in the presence of catalysts.

Thus, *n*-hexane when passed over *chromic oxide* at 460° gives benzene; the reaction involves *cyclization* and *dehydrogenation* (aromatisation).



(6) **Thermal decomposition or cracking or pyrolysis.** The thermal decomposition of organic compounds, in general, is termed *pyrolysis* (*pyros=heat*) and, when applied to paraffins, pyrolysis is known as **cracking**. When heated to about $400-700^\circ$, the paraffins break up into two or more smaller molecules the products depending upon the structure of the paraffin, the pressure under which cracking is carried out, and the presence or absence of a catalyst.

For example,



This process of cracking is extensively employed in converting cheap heavy oils into gasoline or petrol (see chapter XIX)

INDIVIDUAL MEMBERS

METHANE, MARSH GAS, CH_4

Occurrence. Methane is the principal product obtained by the putrefaction of cellulose and other organic matter in swamps and marshes, hence the name **marsh gas**. There the gas is set free by the action of bacteria. Sewage sludge fermented by bacteria yields a gas which contains about 70% methane. It also occurs in coal mines where it mixes with air and on applying a flame explodes violently and hence the name **feuer damp** given to it by coal miners (*feuer*, fire; *damp*, vapour). The *natural gas* issuing from the ground in petroleum regions contains about 85% of methane. Wood gas and coal gas obtained by the dry distillation of wood and coal respectively contain large quantities of methane.

Preparation.

1. **Laboratory methods.** (i) Methane is conveniently prepared in the laboratory by heating a mixture of fused sodium acetate (1 part) and soda lime (4 parts) in a hard glass tube. The gas is collected over water (Fig. 1).

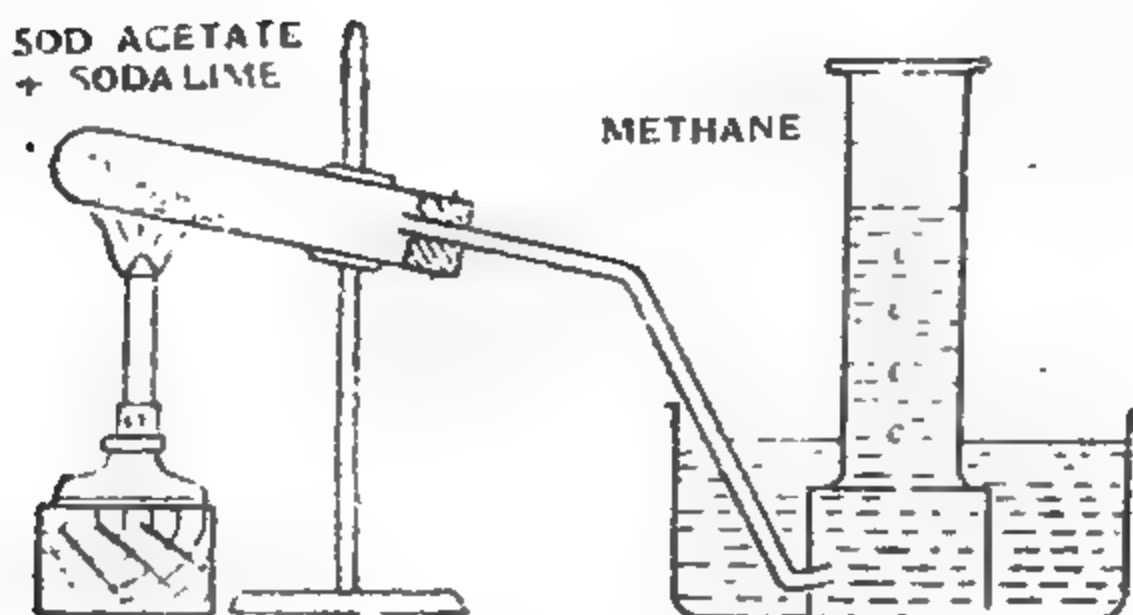
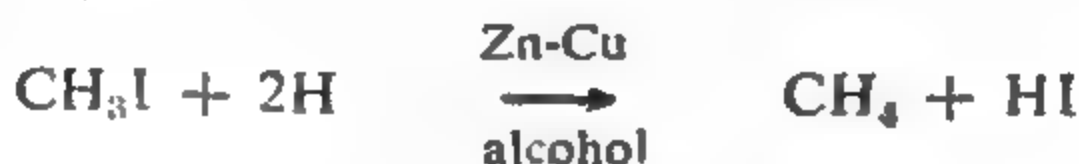


Fig. 1. Preparation of Methane

(ii) Pure methane is obtained readily by the reduction of methyl iodide with nascent hydrogen (obtained from zinc-copper couple and alcohol or water).



The apparatus used is shown in Fig. 2.

About 25 gm. of pure granulated zinc is immersed in a dilute solution of copper sulphate for some time till the zinc gets coated with a film of copper giving the *zinc-copper couple*. The couple so obtained is washed repeatedly with water and finally with alcohol. It is placed in the flask as well as in the U-tube.

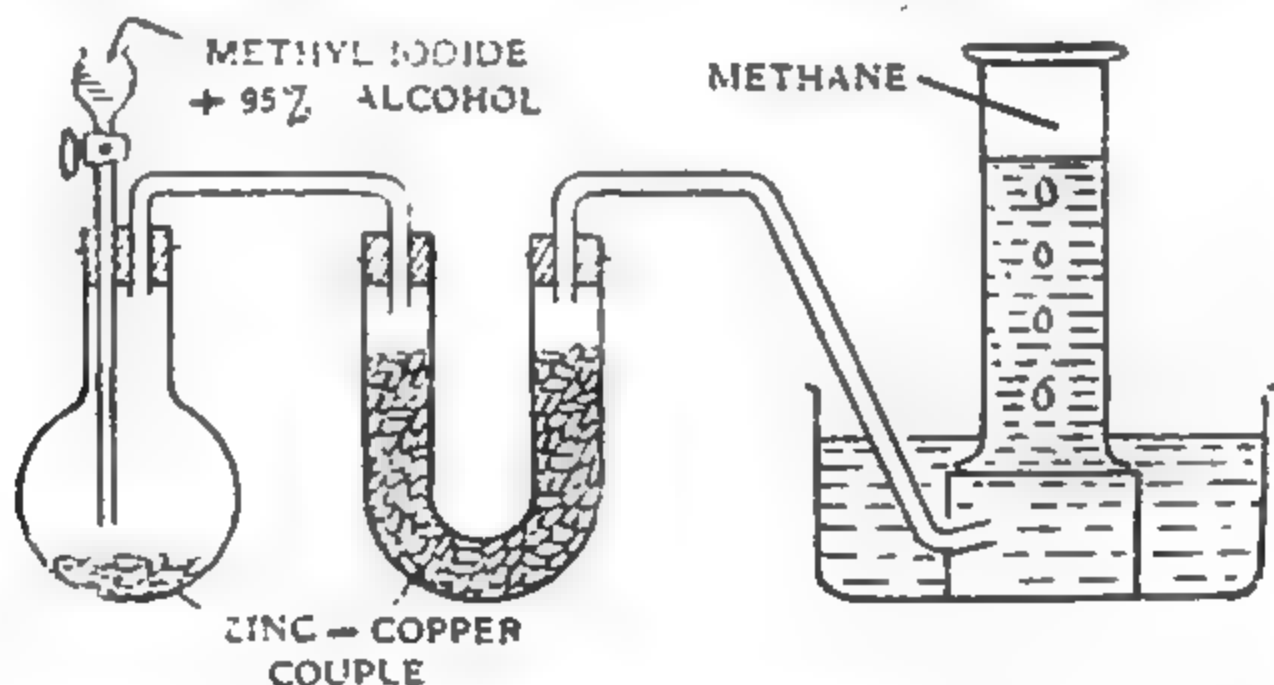


Fig. 2. Preparation of methane.

A mixture of methyl iodide and 95% ethyl alcohol is placed in the dropping funnel and allowed to trickle down gradually. The nascent hydrogen produced by the action of the zinc of the zinc-copper couple on ethyl alcohol



reduces the methyl iodide, in cold, to give methane which is collected over water.

The couple placed in the U-tube removes any methyl iodide vapour coming along with methane.

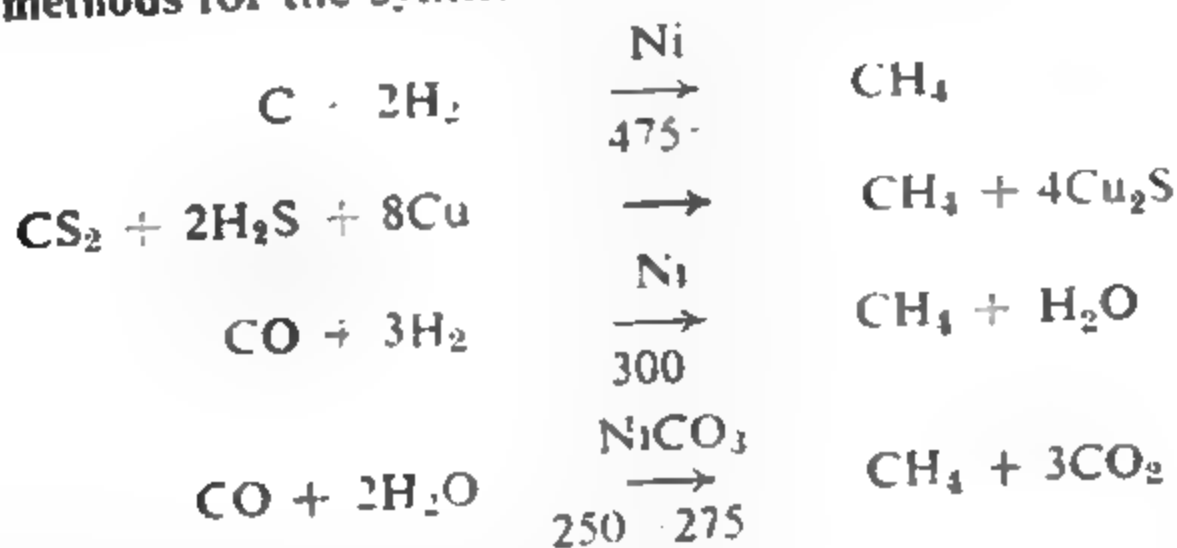
(2) Pure methane can also be prepared by the action of water on methyl magnesium bromide (see general methods of preparation).

(3) Another convenient method is by dropping water on aluminium carbide.



The gas obtained, however, is not pure and contains hydrogen and acetylene as impurities.

Older methods for the synthesis of methane such as



are now only of historical interest.

Physical Properties. Methane is a colourless, odourless, non-poisonous gas which liquefies at -164° at 1 atm. pressure and at 12° under a pressure of 180 atmospheres. It solidifies at -184° . It is only slightly soluble in water but is freely soluble in organic solvents like ether, acetone and alcohol.

Chemical Properties. Methane is neutral in character and is not acted upon by acids or alkalies. It is also inert towards oxidising agents like potassium permanganate or dichromate. The important reactions of methane are :

(1) **Combustibility.** Methane is a combustible gas and burns in air or oxygen with a non-luminous flame, forming carbon dioxide and water.



It *explodes violently* when mixed with air or oxygen and ignited. This is the cause of explosions in coal mines.

(2) **Catalytic oxidation.** (i) Methane can be catalytically oxidised to methanol and formaldehyde (*cf.* general properties of paraffins).

(ii) With ozone, methane is oxidised to formaldehyde.



Since formaldehyde has a characteristic smell, this oxidation reaction is used to *detect the presence of methane*.

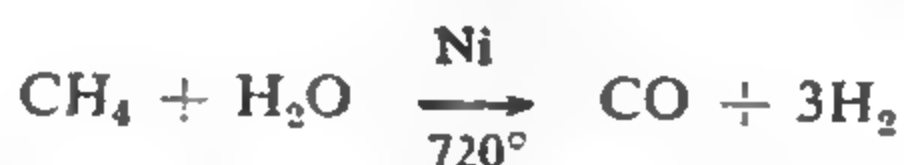
(3) **Halogenation.** Methane can be chlorinated, brominated and iodinated under suitable conditions to give substitution products (*cf.* general properties of paraffins).

(4) **Vapour-phase nitration.** Methane can be converted into nitromethane by vapour phase nitration (*cf.* general properties).

(5) **Decomposition.** When passed through a red hot tube, methane decomposes into carbon and hydrogen.



(6) **Action of steam.** A mixture of methane and steam, when passed over nickel supported on Al_2O_3 at 725° , gives carbon monoxide and hydrogen.



This reaction is used for the *industrial preparation of hydrogen*.

Uses. Methane, available in large quantities as natural gas or produced by the bacterial decomposition of sewage, is now-a-days put to a variety of uses, more important of which are :

(1) *Manufacture of carbon black* which is used in making printer's ink, typewriter ribbons, black paints and in rubber industry for motor tyres to improve their strength and wearing qualities.

(2) *Industrial production of hydrogen* by reaction with steam. The carbon monoxide is eliminated by usual methods.

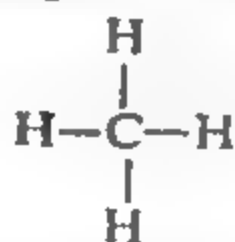
(3) *Manufacture of methanol, formaldehyde, methyl chloride, etc.*

(4) *As a fuel.*

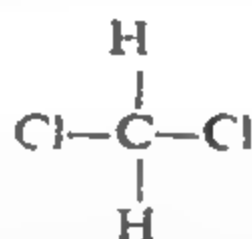
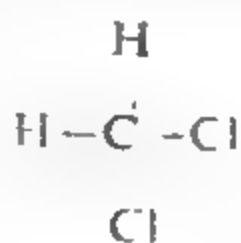
Structure of Methane. (1) The quantitative analysis of methane shows that its molecular formula is CH_4 .

(2) Methane gives only one mono-chloro or mono-bromo or monohydroxy or any other mono substitution product which indicates that all the four hydrogen atoms in its molecule are similar.

Thus methane can be assigned the following structure :



(3) If all the four hydrogen atoms along with the carbon atoms are in one plane, methane should give two dichloromethanes, viz ,



But actually, only one dichloromethane is known showing thereby that methane cannot have a planar formula

(4) Methane is now known to have tetrahedral structure with the carbon atom

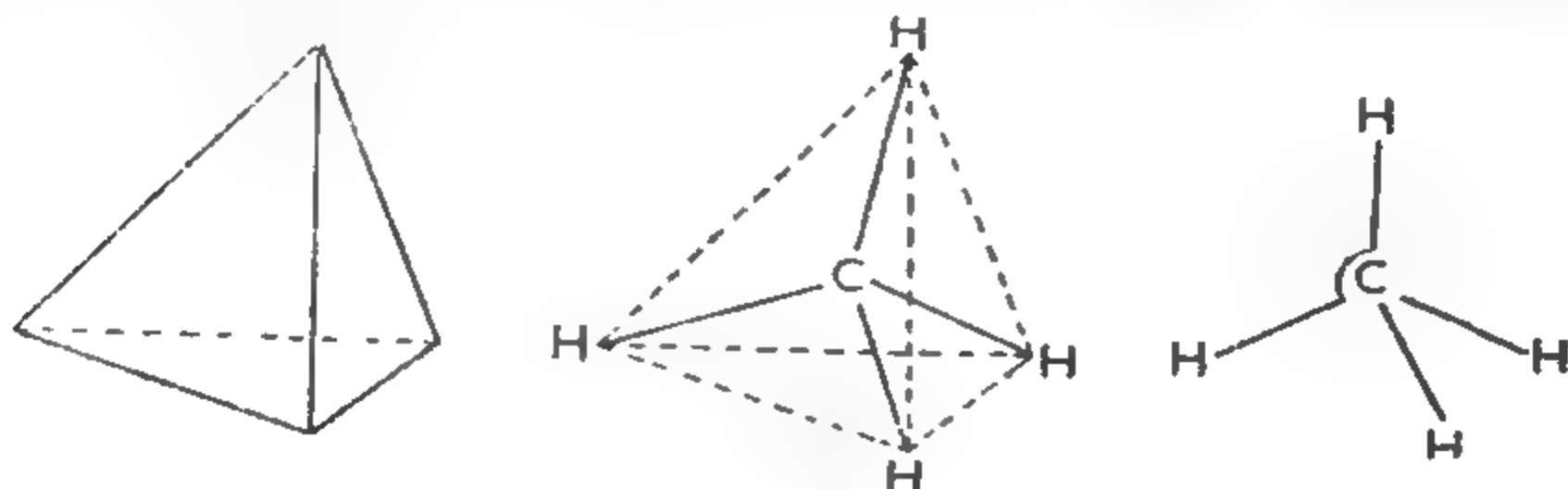


Fig. 3. Tetrahedral structure of methane.

lying at the centre of a regular tetrahedron and the four hydrogen atoms placed at corners (Fig. 3). In this formula, all the hydrogen atoms are symmetrically arranged in space and are exactly identical and thus justify the existence of only one dichloromethane.

The space model of methane is shown in Fig. 2 (page 244) the shaded spheres represent hydrogen atoms.

ETHANE, C_2H_6

Occurrence. Ethane occurs along with methane in natural gas and the gases from the oil wells. Natural gas contains about 10–20% ethane.

Preparation. 1. **Laboratory methods.** (a) Ethane is prepared in the laboratory by the *reduction of ethyl iodide with nascent hydrogen*.



The apparatus and the experimental details are similar to those for the preparation of methane (cf. Fig. 2).

(b) Ethane can also be prepared in the laboratory by the *electrolysis of sodium or potassium acetate solution*. The acetate ions are discharged at the anode giving ethane and carbon dioxide:



Carbon dioxide is absorbed by KOH solution and ethane is collected over water.

The apparatus used for the electrolysis is shown in Fig. 4.

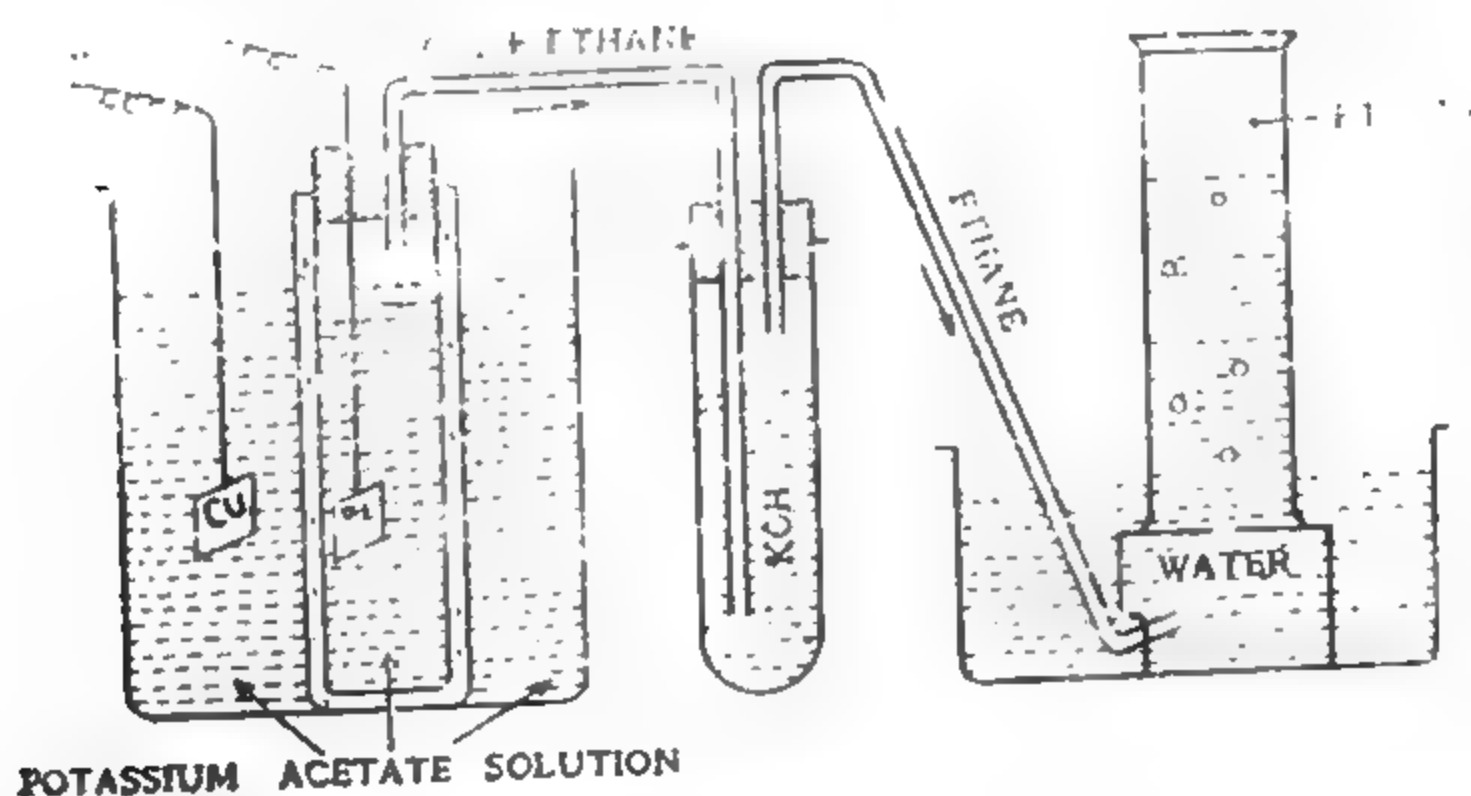
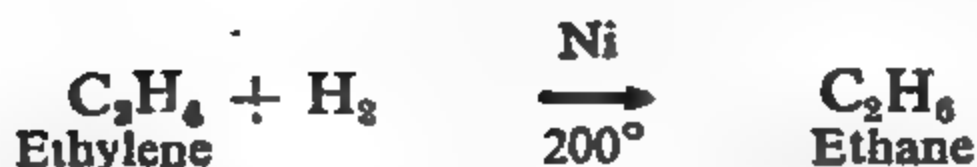


Fig. 4. Preparation of ethane by electrolysis

2. **Industrial Preparation.** Since large amounts of ethylene are now available from the cracking of petroleum, ethane is obtained on an industrial scale by the catalytic reduction of ethylene (Sabatier–Senderen's reaction).



3. Ethane can also be obtained by any of the general methods for the preparation of paraffins.

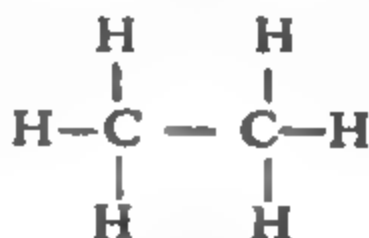
Physical Properties. Ethane, like methane, is a colourless, odourless and tasteless gas but can be liquefied more easily than methane. Liquid ethane boils at -89° and solidifies at -172° . It is practically insoluble in water but dissolves freely in alcohol and other organic solvents.

Chemical Properties. In chemical properties, ethane closely resembles methane. Reagents like sulphuric acid, nitric acid, potassium permanganate, etc., ordinarily have no action. Chlorine and bromine readily attack ethane giving *substitution products*. All the six hydrogen atoms can be successively substituted by the halogen atoms.

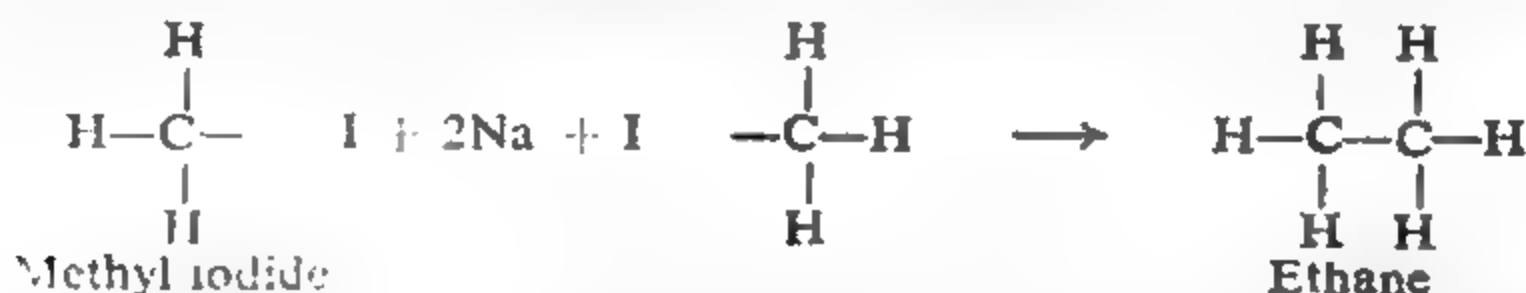
Ethane does not find much use in industry.

Structure of Ethane. (1) Eudiometric analysis shows that the molecular formula of ethane is C_2H_6 .

(2) The two atoms of carbon must be linked directly because the union through a monovalent hydrogen atom is not possible. Assuming tetravalency of carbon, the only possible structure for ethane is



This view is confirmed by its synthesis from methyl iodide by the Wurtz reaction :



(3) Again the structure is not monoplanar. Ethane consists of two tetrahedra joined

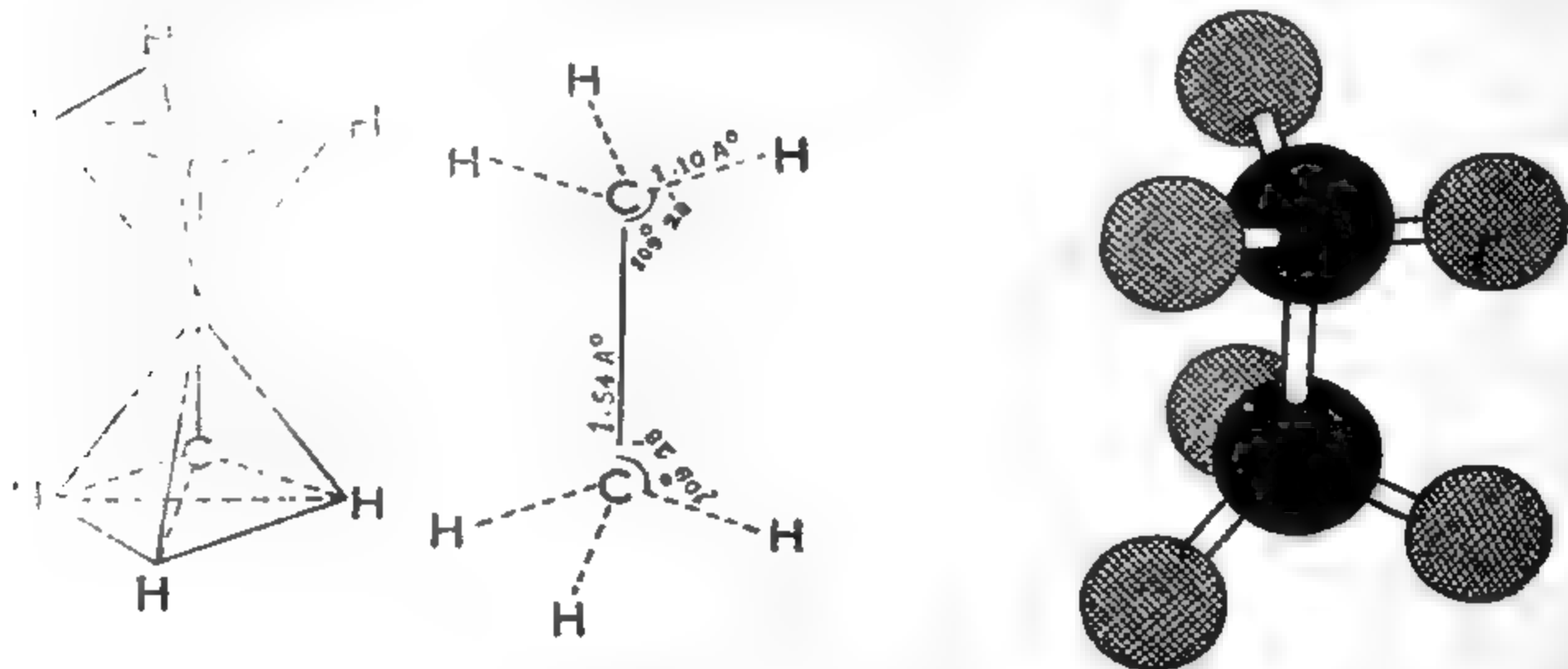
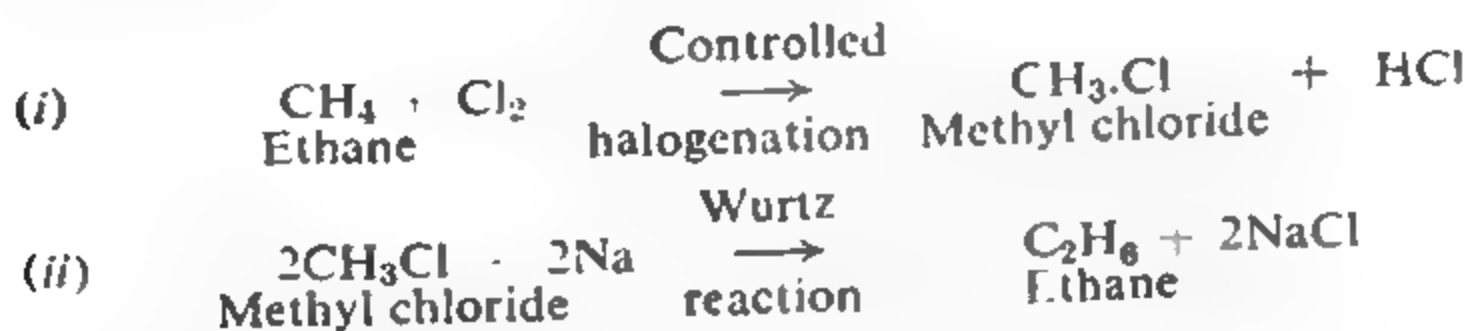


Fig. 5. Tetrahedral structure and space model of ethane.

corner to corner, the remaining six corners being occupied by hydrogen atoms as represented in Fig. 5. The space model of ethane is also shown in the same figure. The shaded spheres represent hydrogen atoms.

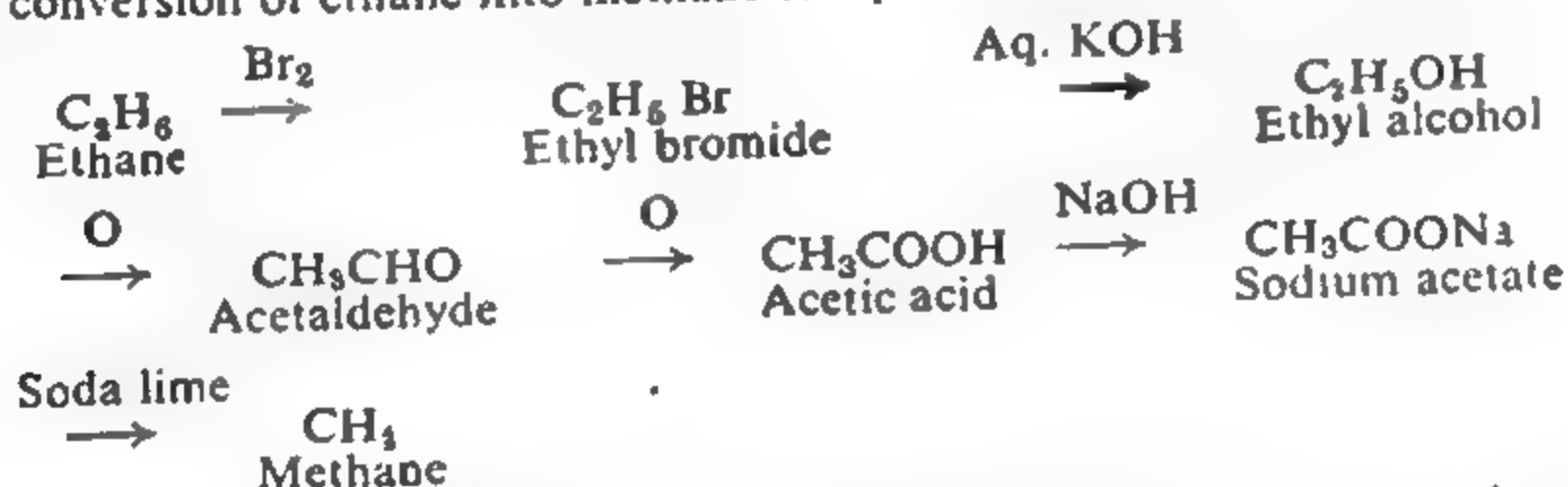
Conversion of Methane into Ethane

The conversion of methane into ethane may be represented by the following equations :



Conversion of Ethane into Methane

The conversion of ethane into methane is represented by the following equations :

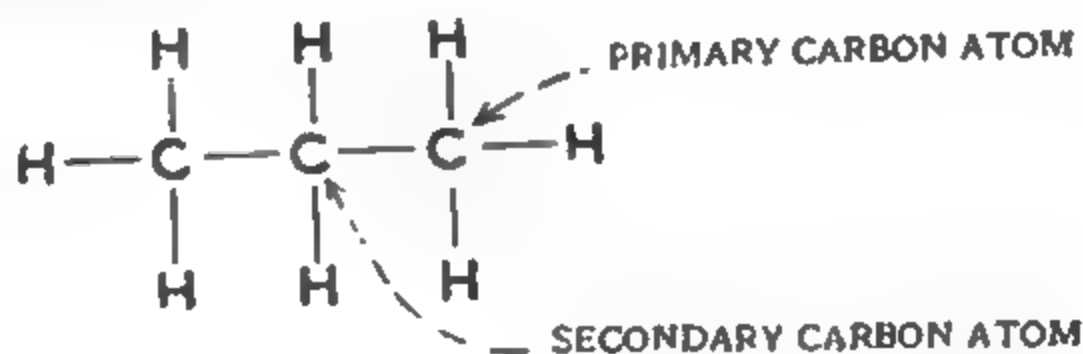


Isomerism in Paraffins. As already mentioned, in organic chemistry, the same molecular formula may stand for more than one compounds which differ from one another in physical as well as in chemical properties. This phenomenon is known as **isomerism**. In the case of hydrocarbons, the isomerism originates from the difference in the structures of the carbon chains. This type of isomerism is known as the **chain isomerism**.

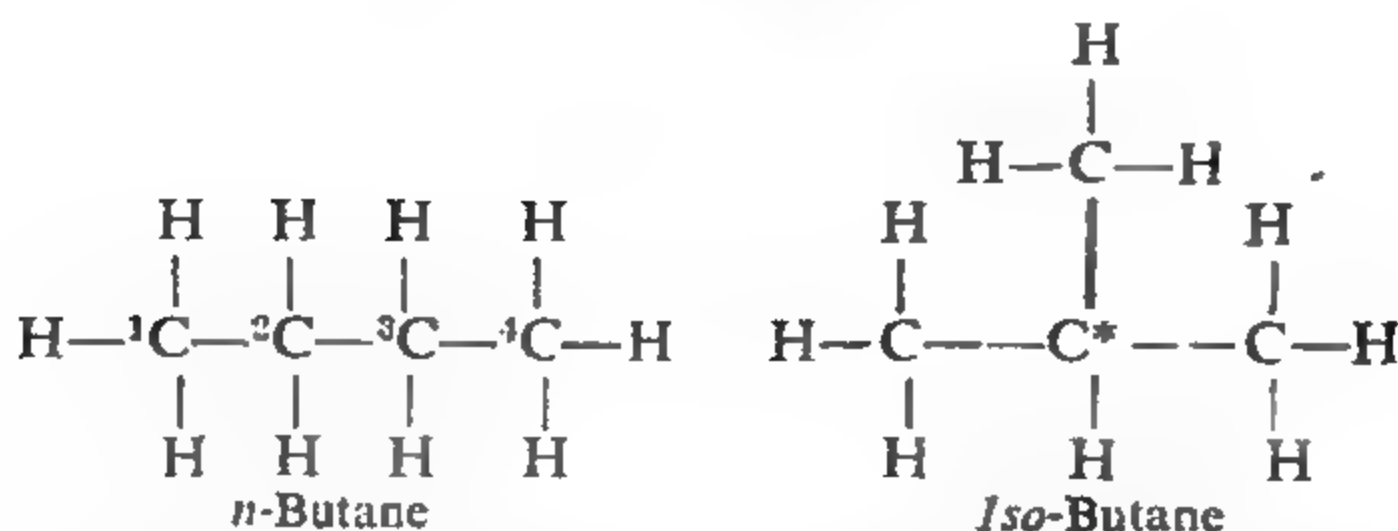
The first three members of the paraffin series, viz., methane, ethane and propane are simple and exist only in one form.

Butane exists in two isomeric forms. This will be clear from the following discussion :

In propane, the three carbon atoms are not all alike. The end carbon atoms are *primary* (attached to one other carbon atom) while the middle one is *secondary* (attached to two other carbon atoms), as shown below :

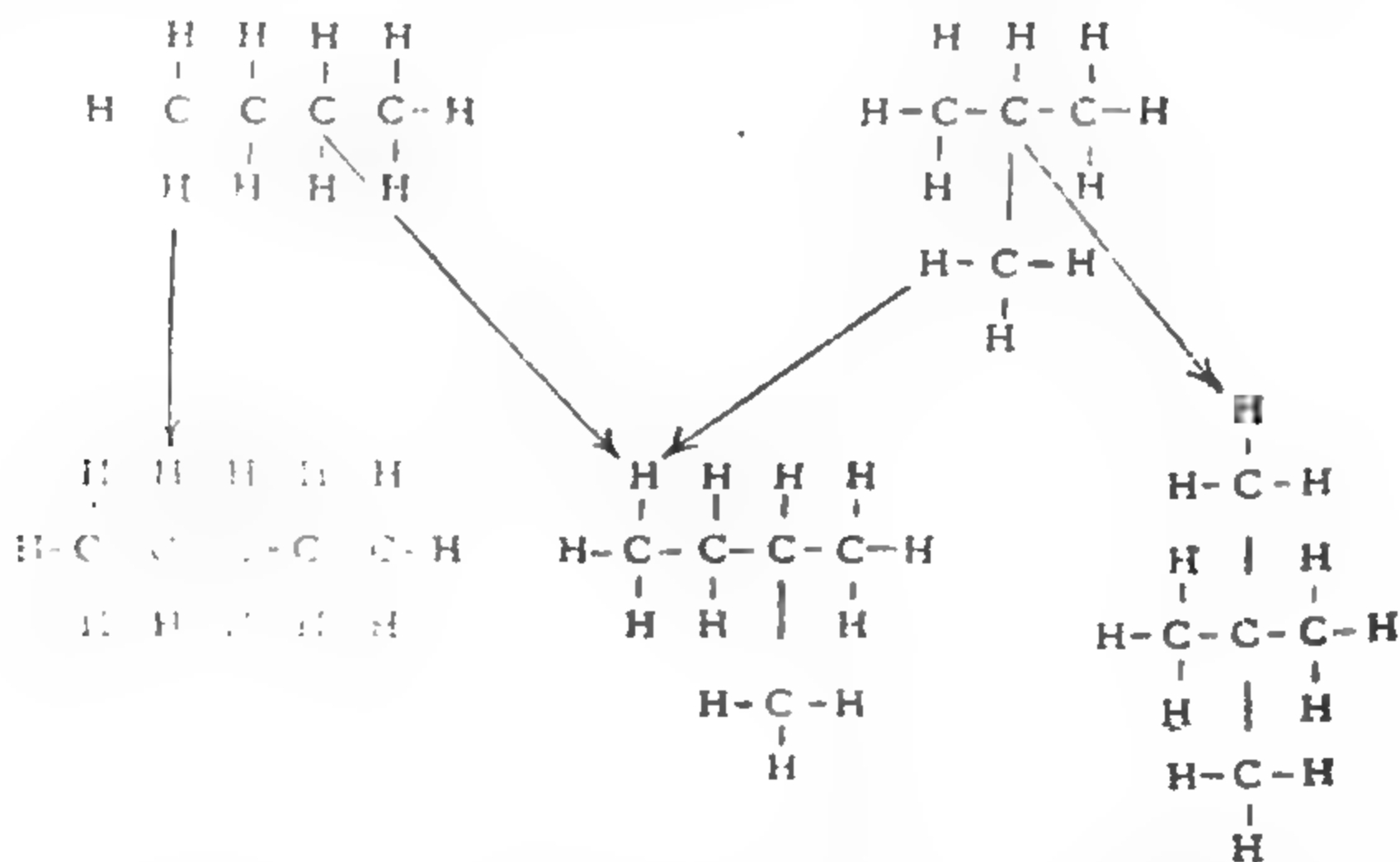


Therefore, the butane obtained by adding the fourth carbon atom at the primary position will be different from the butane obtained by adding the same at the secondary position as shown below, the thick line representing the bonding of the fourth carbon atom :



Both the butanes are known ; the boiling point of *n*-butane is -0.5° and that of *iso*-butane is -12° .

Further, in normal butane, the end carbon atoms (1 and 4) are *primary* and the middle ones (2 and 3) are *secondary*. In *iso*-butane, the end carbon atoms are primary while the remaining one (marked with an asterisk) is *tertiary*, *i.e.*, attached to three carbon atoms. Thus, normal and isobutanes together contain three types of carbon atoms, *viz.*, primary, secondary and tertiary and, therefore, three different pentanes are expected according as the new carbon atom is attached to a primary or a secondary or a tertiary carbon atom of butanes, as illustrated below :



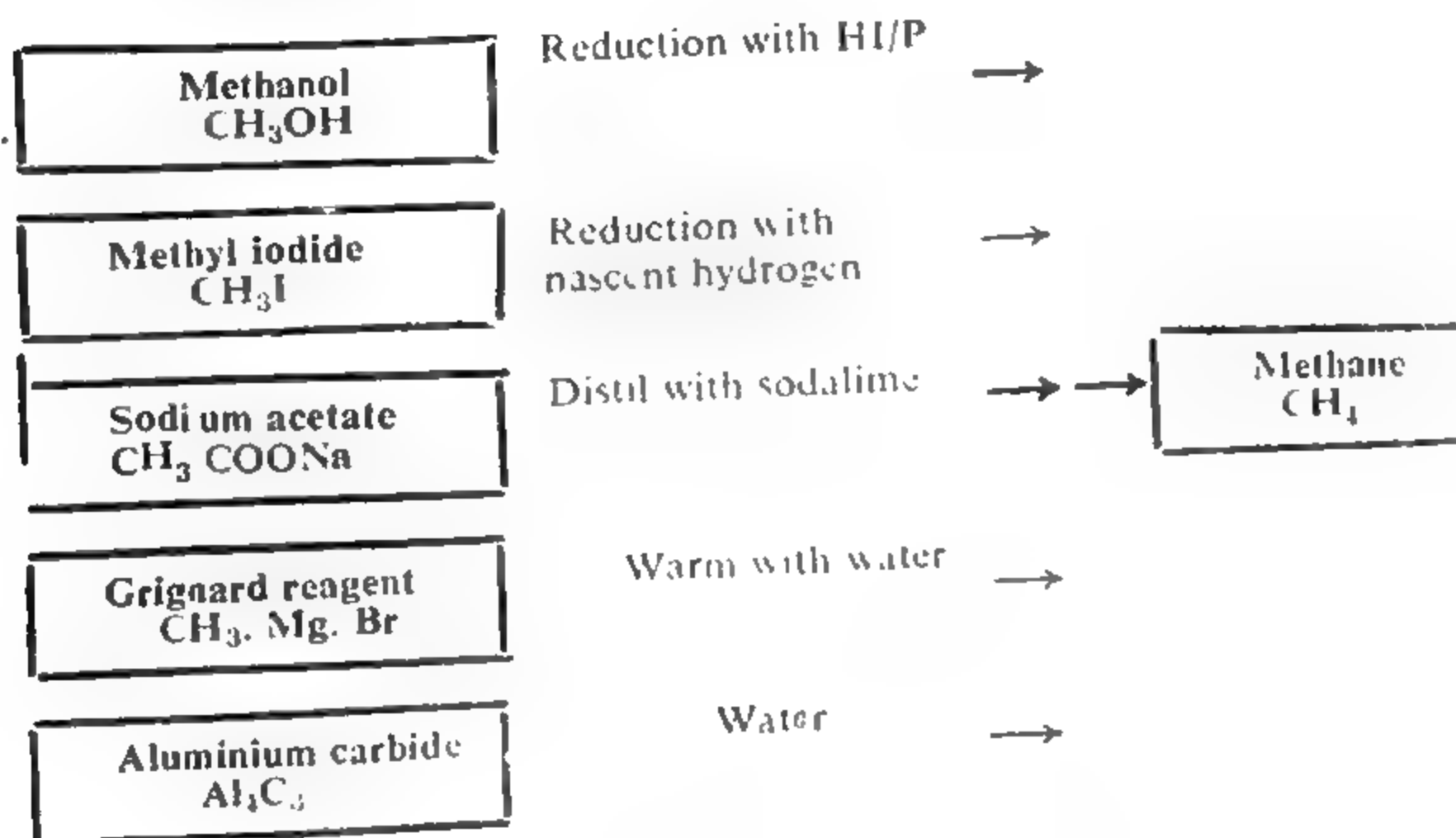
n-Pentane (b. p. 360) *iso*-Pentane (b.p. 28°) *neo*-Pentane (b.p. 9.4°)

If the three pentanes are known.

With the increase in the number of carbon atoms, the number of isomers goes on increasing. Thus, there are 5 hexanes, 9 heptanes, 18 octanes, 35 nonanes, 75 decanes and so on. But in most cases very few of them have been actually prepared and studied.

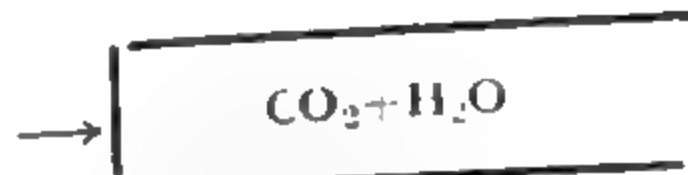
SUMMARIES OF TYPICAL MEMBERS

Preparation.

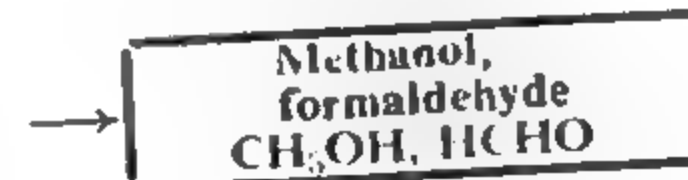


Properties.

Combustion



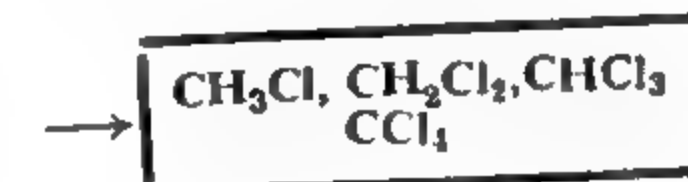
Oxidation with ozone

Vapour phase nitration
475°Catalytic oxidation
Cu or MoO

Steam, (Ni, 725°)



Decomposition (1000°)

Chlorination
diffused sunlightMethane
 CH_4

2. PREPARATION AND PROPERTIES OF ETHANE

Preparation.

Ethyl alcohol C_2H_5OH	Reduction with HI/P \longrightarrow	
Ethyl iodide C_2H_5I	Reduction with nascent hydrogen ($Na + C_2H_5OH$) \longrightarrow	
Sodium propionate C_2H_5COONa	Distil with sodalime \longrightarrow	Ethane C_2H_6
Grignard reagent C_2H_5MgBr	Warm with water \longrightarrow	
Pot. acetate CH_3COOK	Electrolysis \longrightarrow	
Methyl iodide CH_3I	Na metal in ether solution (Wurtz reaction) \longrightarrow	

Properties.

Ethane C_2H_6	Catalytic oxidation Cu or MoO \longrightarrow	Acetaldehyde, Acetic acid CH_3CHO, CH_3COOH
	Combustion \longrightarrow	$CO_2 + H_2O$
	Vapour phase nitration \longrightarrow	Nitroethane $C_2H_5NO_2$
	Chlorination (diffused sun) \longrightarrow	$C_2H_5Cl, C_2H_4Cl_2, \dots, C_2Cl_6$

QUESTIONS

- What are hydrocarbons and how are they classified?
- Describe the general methods for the preparation of saturated hydrocarbons. What is meant by substitution reactions?
- Describe four methods for the preparation of paraffins. Explain under what conditions the paraffins react with (i) halogens (ii) nitric acid (iii) sulphuric acid (iv) oxygen.
- Write short notes on :
 - Vapour phase nitration of paraffins.
 - Aromatization.
 - Cracking,

5. How is methane prepared in the laboratory ? Under what conditions can it be (i) chlorinated (ii) nitrated (iii) oxidised into methanol ?
 6. How is pure methane prepared in the laboratory ? Explain how can it be converted into (i) ethane (ii) methyl alcohol (iii) formaldehyde (iv) nitromethane ? How has the structure of methane been established ?
 7. Give the methods for the preparation of ethane. How does it react with halogens ?
 8. Describe the preparation and properties of methane. To what uses is it put ?
 9. What is meant by Isomerism ? Discuss the isomerism of butanes and pentanes.
 10. How is methane prepared in the laboratory ? What are its chief properties ? "Methane is a saturated hydrocarbon". Explain this statement. (*Panjab Inter 1949*)
 11. "Methane is a *saturated* compound and all the hydrogen atoms in its molecule are *equivalent*". Justify the above statement. (*U.P. Board Inter 1953*)
 12. Discuss (giving equations and names of the products) the action of water on :
 (i) Aluminium carbide.
 (ii) Magnesium ethyl bromide. (*Panjab Inter 1949*)
 13. Describe any three methods for the preparation of aliphatic saturated hydrocarbons. (*Panjab Inter 1951*)
 14. Describe the general methods for the preparation of saturated hydrocarbons. (*Delhi Pre. Engg. 1960*)
 15. Give the structural formulae of the first five alkanes and develop the idea of chain isomerism.
 16. Give general methods of preparation and properties of the paraffins and discuss the isomerism of butanes. (*Jammu and Kashmir Inter 1955*)
 17. "All the four valencies of carbon are alike". Offer a proof in support of this statement. (*Panjab Inter 1961*)
 18. Fill in the blanks :
 (i) Alkanes are highly——compounds.
 (ii) Wurtz's reaction consists in——in the presence of ——metal in dry ether
 (iii) Primary, secondary and tertiary carbon atoms are those which are linked to——, ——and——carbon atoms respectively.
 (iv) Alkanes show a type of isomerism known as——isomerism.
 (v) The vapour phase nitration of methane yields——.
 (vi) Ethane can be —— in the presence of diffused sunlight to yield ——
 (vii) A mixture of——and——has been extensively used for reducing ——to alkanes.
-

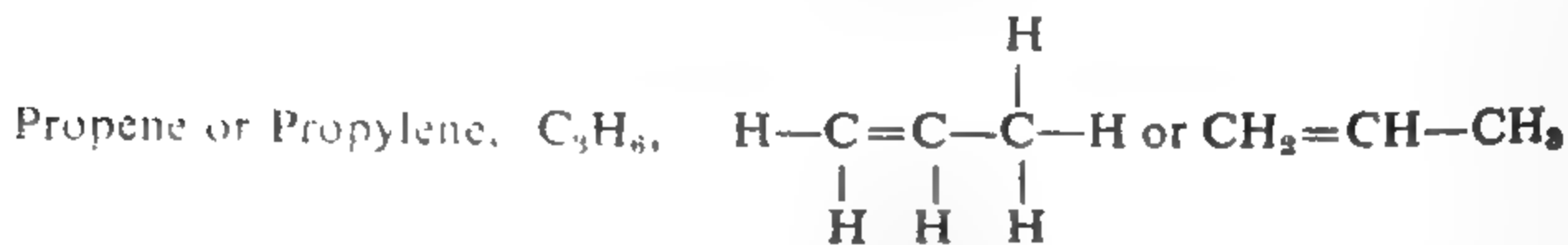
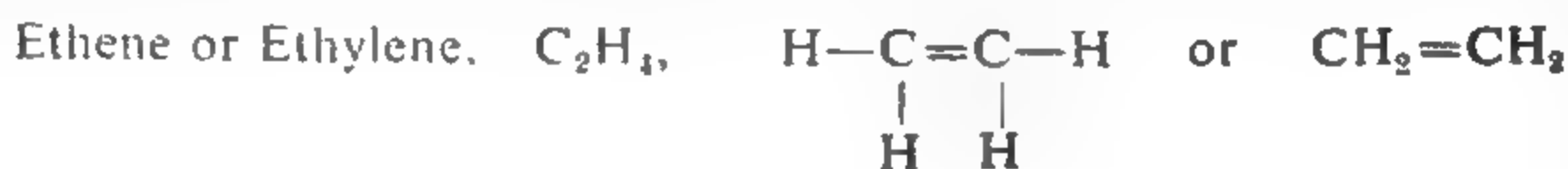
CHAPTER XXVI

UNSATURATED HYDROCARBONS (ALKENES OR OLEFINS)

Unsaturated Hydrocarbons. These are compounds of carbon and hydrogen in which all the valencies of carbon atoms are not fully satisfied by hydrogen atoms. There are two main types of unsaturated hydrocarbons, namely the alkenes and the alkynes. Alkenes are discussed in this chapter. Alkynes will be taken up in the next chapter.

ALKENES

Alkenes are those unsaturated hydrocarbons which contain two hydrogen atoms less than the corresponding paraffins. They are also known as ethylenes after the name of the first member (ethylene) of the series or olefins (as the first member, ethylene, forms an oily product with chlorine ; *olefiant* = oil forming). Each alkene contains one double bond in the molecule. For example,



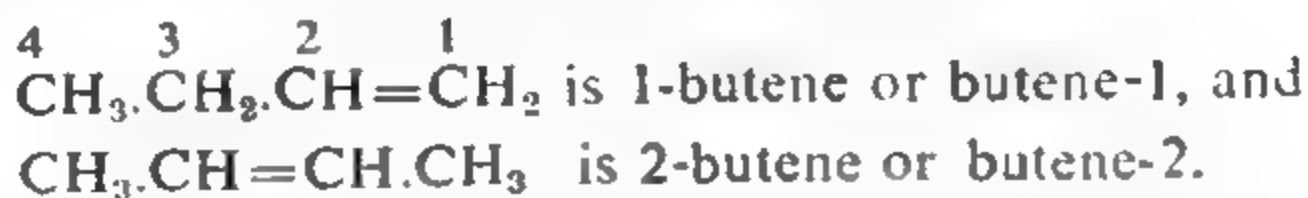
The general formula of the series is $C_n.H_{2n}$.

Nomenclature. The alkenes are named by changing the suffix *-ane* of the corresponding alkane by *-ylene*, e.g.,

<i>Formula of the alkene</i>	<i>Name of the corresponding alkane</i>	<i>Name of the alkene</i>
$CH_2=CH_2$	Ethane	Ethylene
$CH_3.CH=CH_2$	Propane	Propylene
$CH_3.CH_2.CH=CH_2$	Butane	Butylene
$CH_3.CH_2.CH_2.CH=CH_2$	Pentane	Pentylene

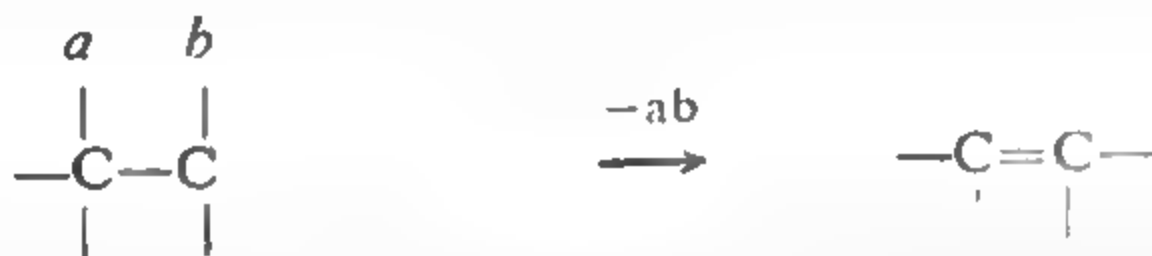
In the I. U. C. system of naming the alkenes, the longest chain of carbon atoms carrying the ethylenic linkage is selected and the carbon atoms are

numbered in such a way that those containing the double bond have the least possible number, e.g.,



Evidently, the position of the double bond is indicated by prefixing or suffixing the number of the carbon atom preceding the double bond.

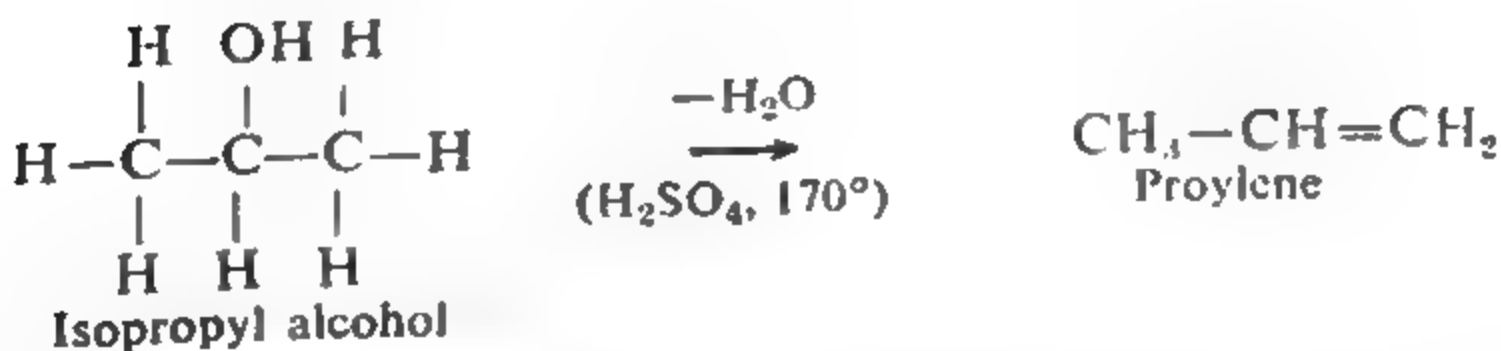
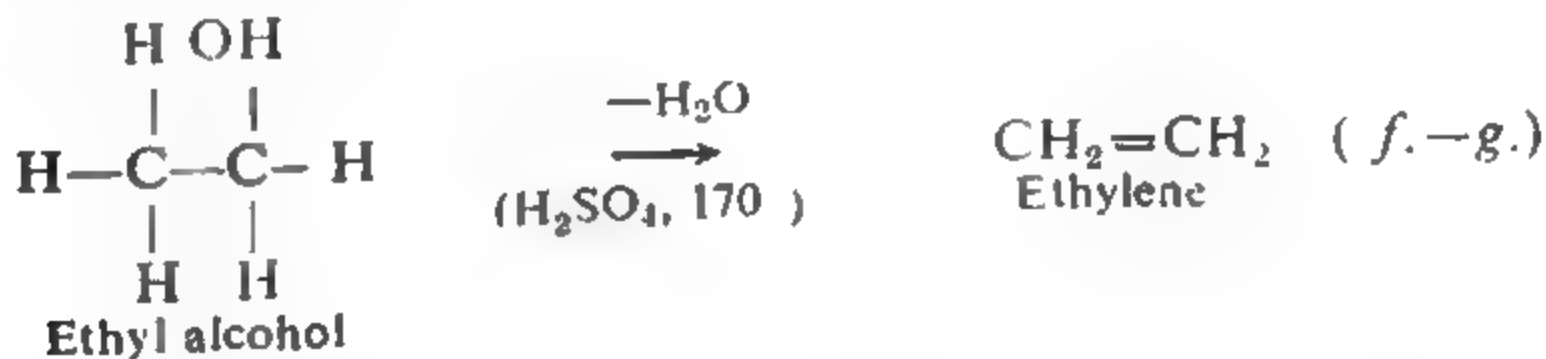
General Methods of Preparation. Almost all the methods of preparation of olefins involve the removal of atoms or groups from adjacent carbon atoms of a chain resulting in the creation of a double bond,



where 'a' and 'b' may be the same or different. The actual conditions and reagents required for the removal of 'a' and 'b' depend upon the nature of the atoms or groups to be removed.

The general methods for the preparation of olefins are :

1. Dehydration of alcohols. Lower olefins are conveniently prepared in the laboratory by the dehydration of alcohols. For example,

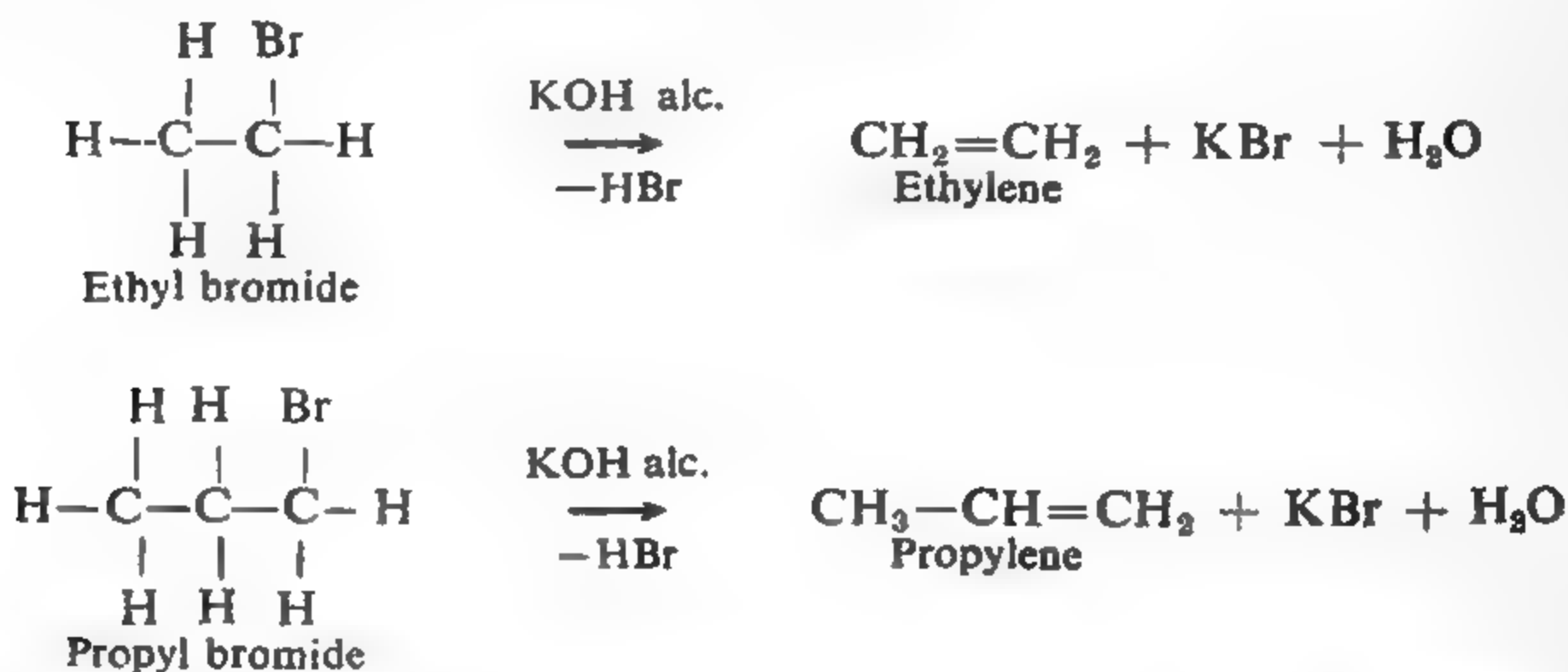


The **dehydrating agents** used for the purpose are : *concentrated sulphuric acid, phosphoric acid, zinc chloride or heated alumina.*

Recent work has established that olefins are produced by the following steps :

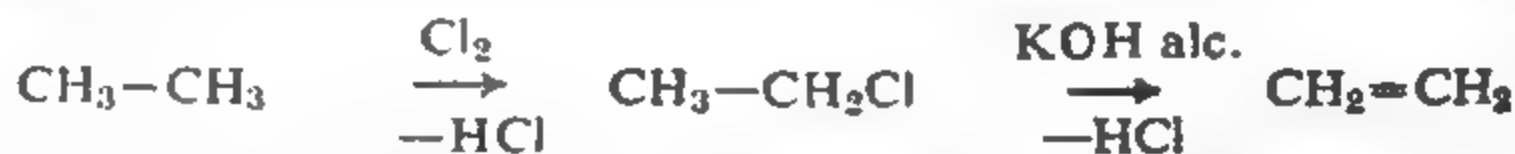


2. Action of alcoholic potash on alkyl halides. When an alkyl halide is heated with an alcoholic solution of potassium hydroxide (alcoholic potash), a molecule of the halogen acid is eliminated resulting in the formation of the corresponding olefin. For Example,



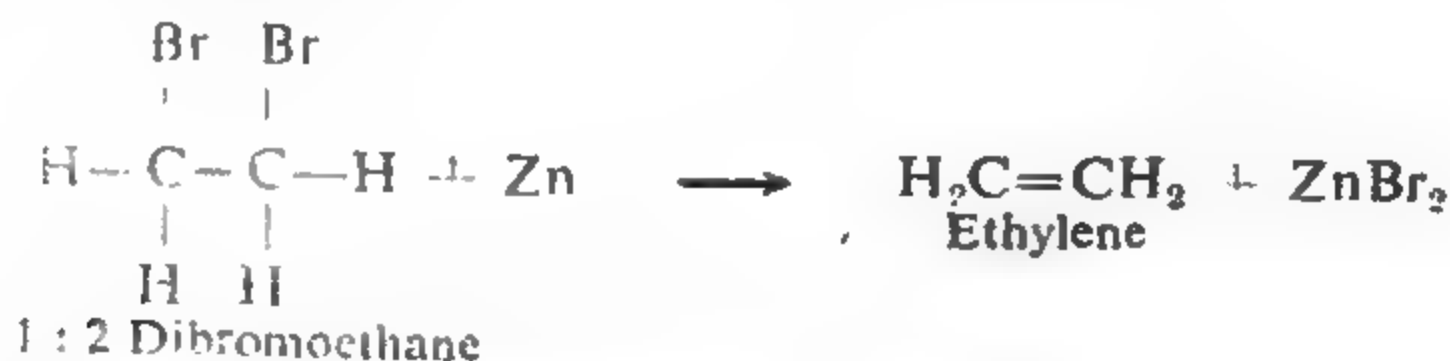
This method is more suitable for preparing higher olefins. In case of ethylene, the yield is so small that this method cannot be used in laboratory.

However, this is a very suitable method for introducing a double bond in an organic compound, *e.g.*,



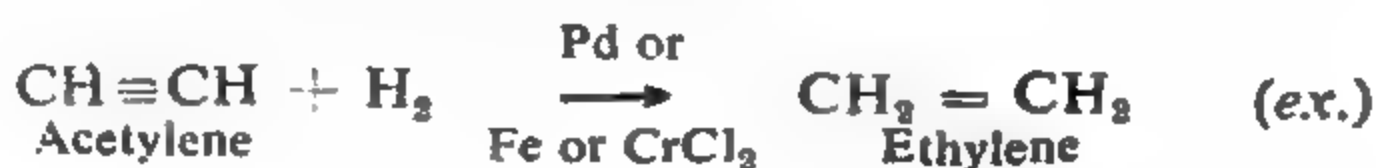
The mechanism of dehydrohalogenation is similar to that of dehydration.

3. Heating dihalogen derivatives with zinc. Olefins can be easily prepared by treating dihalogen derivatives of alkanes, having the two halogen atoms attached to adjacent carbon atoms, with active metals such as finely divided zinc or magnesium. For example,

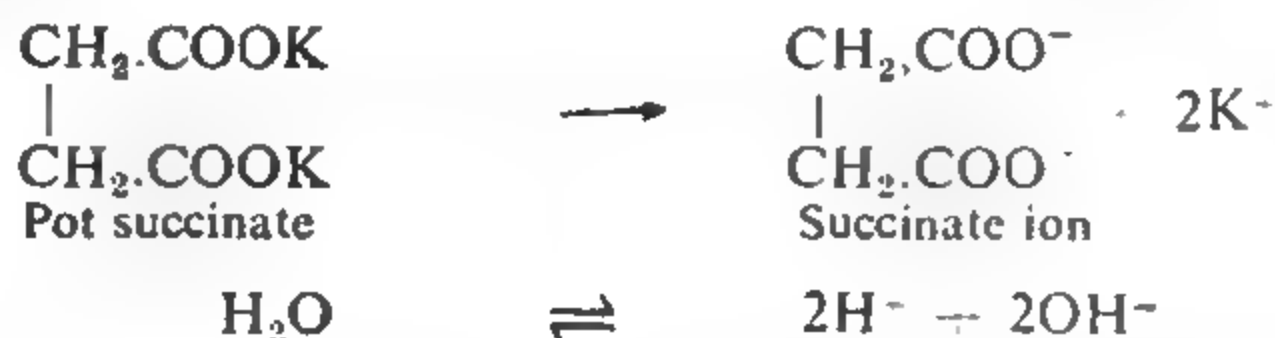


This method is seldom used as the *vic.* dihalides are not freely available.

4. Controlled reduction of acetylene hydrocarbons. When a mixture of acetylene and hydrogen is passed over palladium or iron or chromous chloride, the partial reduction of acetylene yields ethylene.

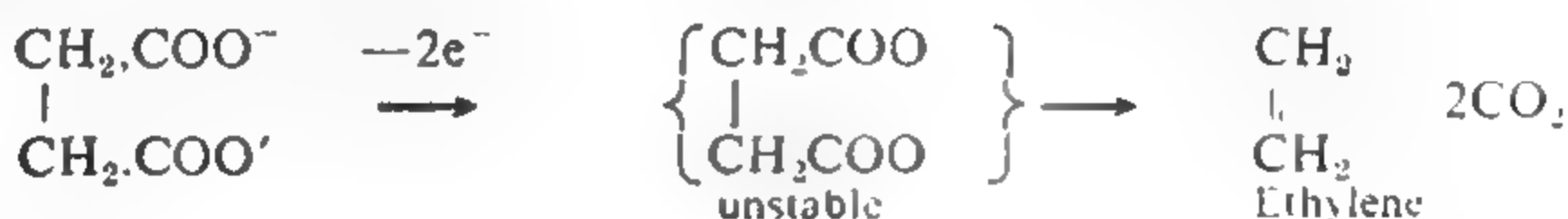


5. Electrolysis of alkali salts of dicarboxylic acids. Ethylene can be conveniently prepared by the electrolysis of sodium or potassium salt of succinic acid.



At anode.

The negative acid ion goes to the anode and gets decomposed into the alkene and carbon dioxide,



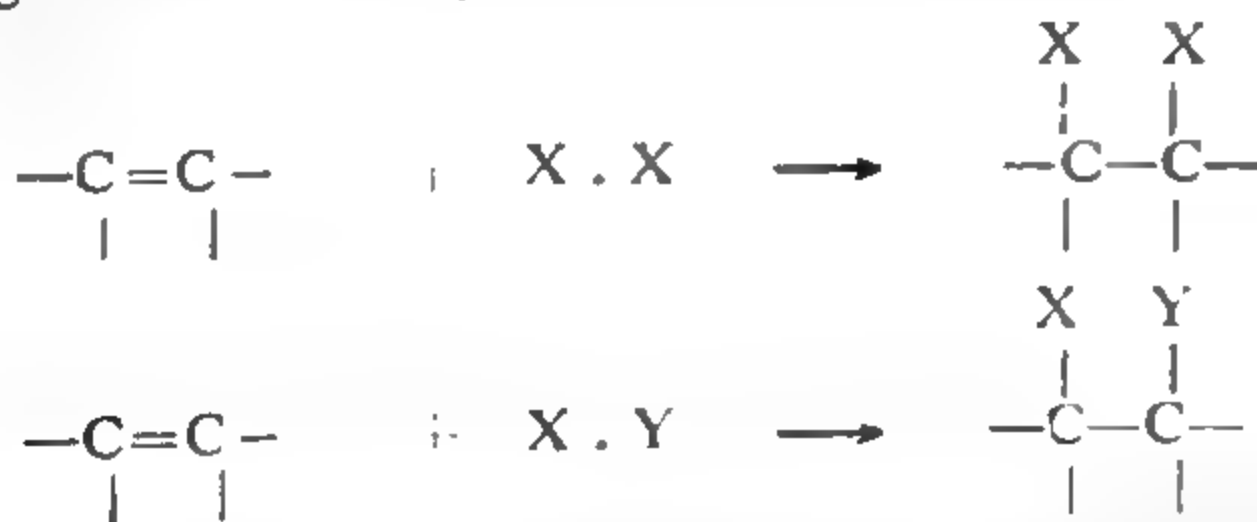
At cathode.

The hydrogen ions get discharged liberating hydrogen.



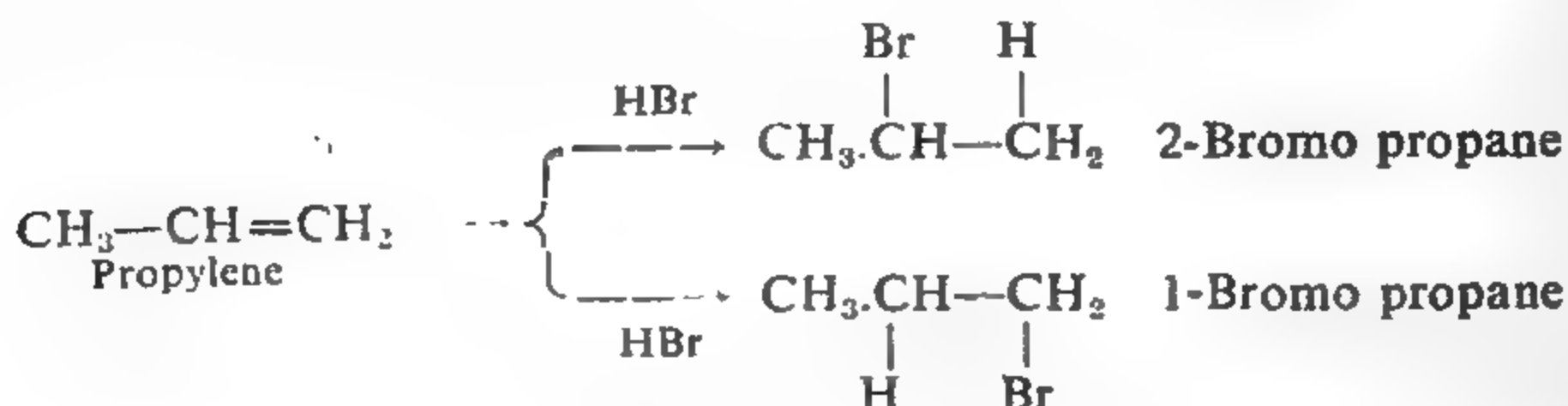
Physical Properties. In physical characteristics, the olefins resemble paraffins. The first three members are gases, the next fourteen liquids, and the higher ones are solids. They are all colourless and odourless (excepting ethylene which has a pleasant smell) compounds, practically insoluble in water but freely soluble in alcohol, ether, etc. Other physical properties such as melting point, viscosity and specific gravity increase fairly regularly with rise in molecular weight.

Chemical Properties. (1) **Addition Reactions.** Unlike paraffins, the olefins are highly reactive compounds, their unsaturated nature being responsible for their great chemical reactivity. This is shown by the fact that the olefins readily form **addition products** with a variety of substances such as hydrogen, halogens, halogen acids, ozone, etc. The addition of the incoming atoms or molecules takes place at the double bond yielding saturated compounds with the simultaneous conversion of a double bond into a single bond*. Thus,



*The normal addition of halogens, halogen acids, etc., to the double bond is not so simple as shown above. It is a two step process, involving the formation of an intermediate 'carbonium ion'. The complete mechanism is, however, beyond the scope of the present volume. The interested reader may refer to authors' Vol. II.

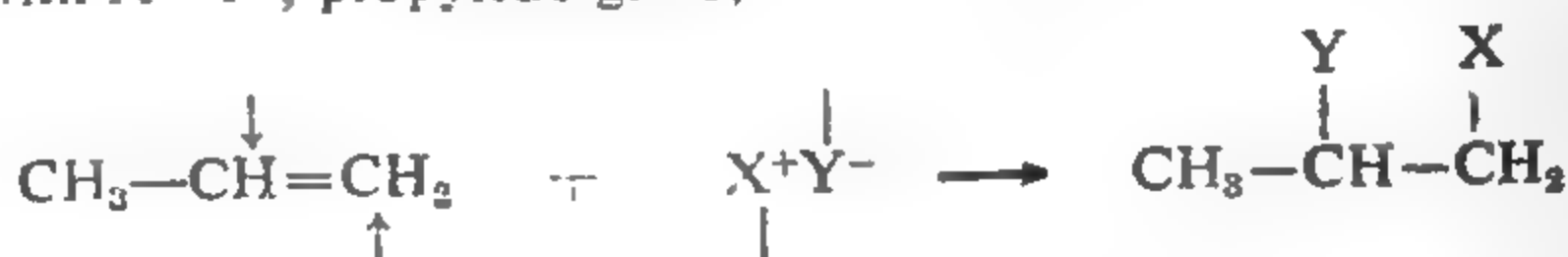
The addition of reagents like XY (e.g., HCl , HBr , $HClO$) to an unsymmetric olefin, for example, propylene ($CH_3-CH=CH_2$), can take place in two different ways, giving two different products :



In actual practice, the main product is 2-bromopropane. This is in accordance with an empirical generalization known as **Markownikoff's rule*** which states that

"In a normal addition, the negative part of the molecule adding to the double bond goes to that carbon atom which carries smaller number of hydrogen atoms."

Thus, with $X^+ Y^-$, propylene gives,



(2) **Polymerisation.** Under suitable conditions of temperature and pressure and in the presence of a suitable catalyst, olefins readily undergo polymerisation, i.e., two or more molecules combine to give a single complex molecule.



For example, ethylene in the presence of sulphuric acid at high temperature polymerises to give compounds of formulae, $C_{10}H_{20}$, $C_{15}H_{30}$, etc.

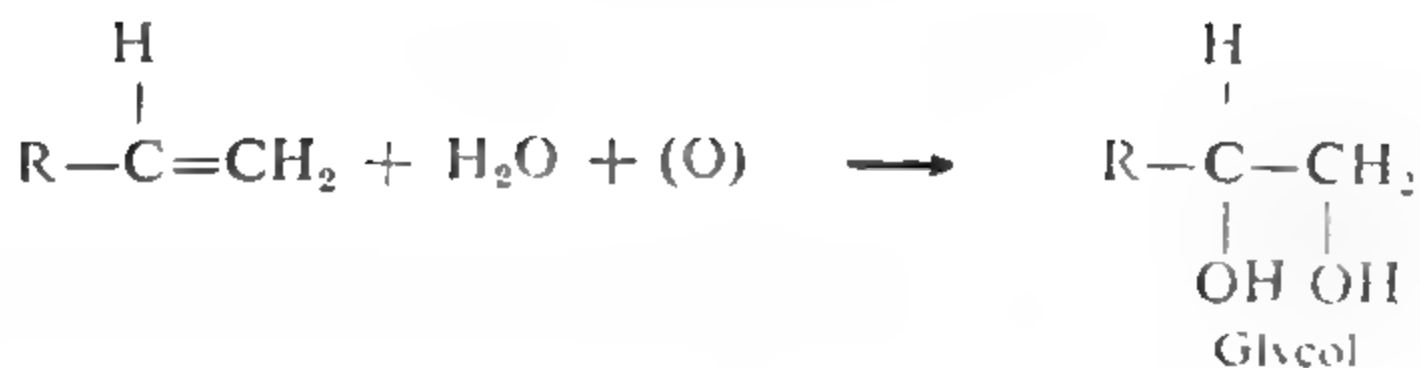
(3) **Oxidation Reactions.** Unlike paraffins, the olefins are easily attacked by oxidising agents like potassium permanganate, potassium dichromate, nitric acid, etc., giving different products under different conditions of oxidation.

Thus,

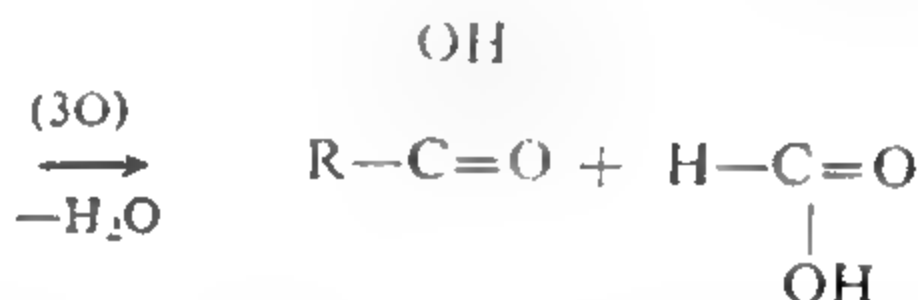
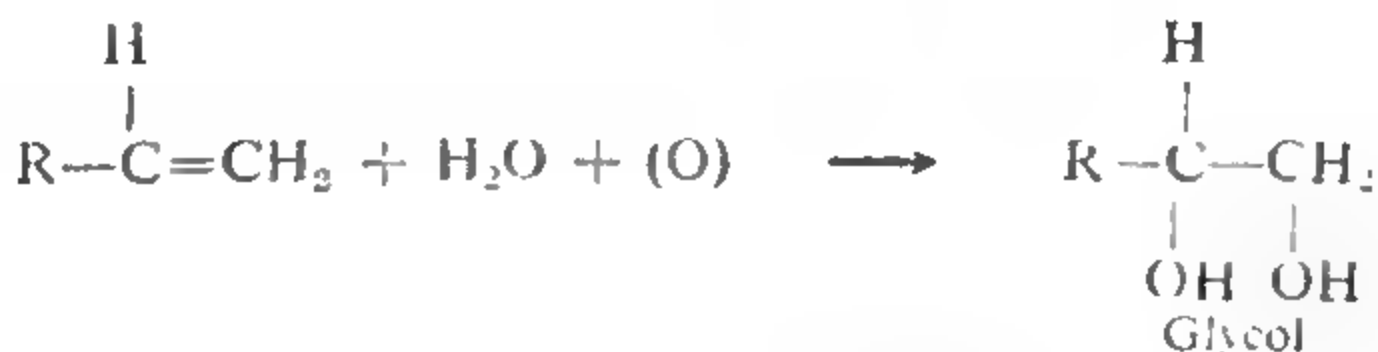
With alkaline potassium permanganate or hydrogen peroxide, we get glycol.

The Markownikoff's rule is not of universal application. Many exceptions are known. For instance, addition of HBr to propylene in the presence of organic peroxides does not follow Markownikoff's rule.





and with acidic potassium permanganate, we get acids.



ETHYLENE, ETHENE, C_2H_4 , $\text{CH}_2=\text{CH}_2$

Ethylene is the first member of the series. Methylene (CH_2), corresponding to methane, does not exist in the free state and is merely a radical known as methylene radical.

Occurrence. Ethylene occurs to the extent of about 20 per cent in *natural gas*. It is also present in small amounts in coal gas and wood gas. Large amounts of the gas are obtained by the cracking of petroleum.

Preparation. Ethylene can be prepared by any of the general methods described above.

Laboratory Preparation. (1) Ethylene is conveniently prepared in the laboratory by heating a mixture of ethyl alcohol and concentrated sulphuric acid to about $160-170^\circ$, in the presence of a *small amount of anhydrous aluminium sulphate*. The reaction takes place in two stages ;



The apparatus used is shown in Fig. 1.

A mixture, consisting of 50 ml. ethyl of alcohol, 100 ml. of concentrated sulphuric acid and about 8 gm. of anhydrous aluminium sulphate, is placed in the flask and about 50 gm. of sand added in order to avoid frothing. The flask is heated on a sand bath to about 170° when a steady current of ethylene is obtained. The gas so obtained

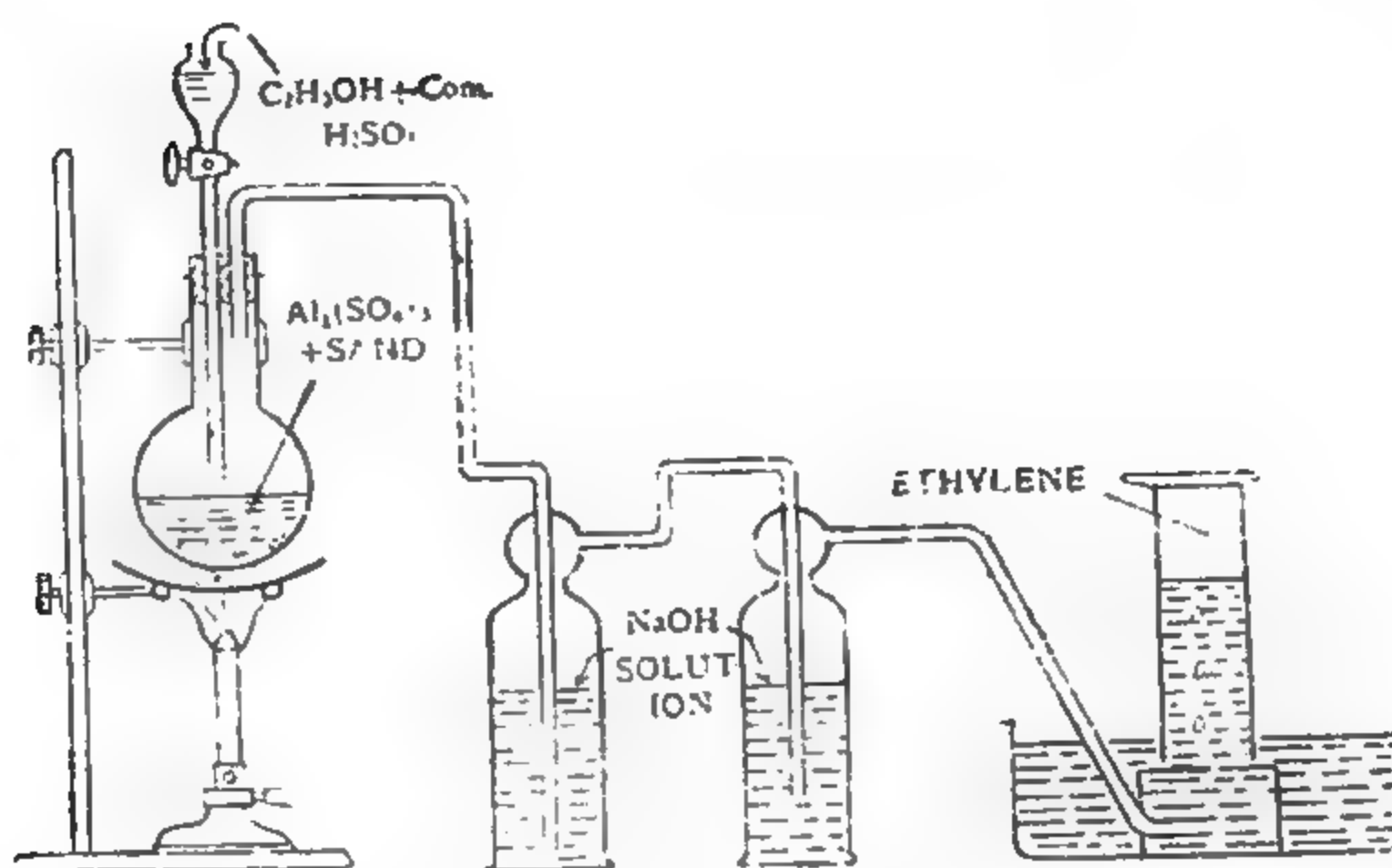
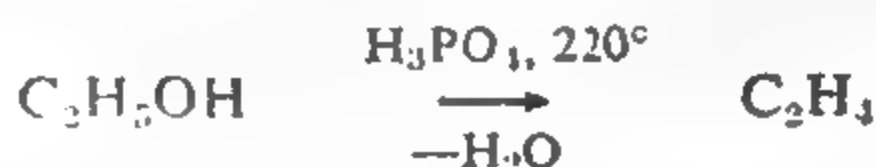


Fig 1. Preparation of ethylene

is usually contaminated with *sulphur dioxide, *carbon dioxide, and vapour of *ether and alcohol. These impurities are eliminated by passing the gas successively through well cooled empty wash bottles (not shown) where the vapours of alcohol and ether are condensed and then through wash bottles containing a solution of sodium hydroxide which absorbs carbon dioxide and sulphur dioxide. Pure ethylene is collected over water.

(2) Another method of preparing pure ethylene in the laboratory is by dropping ethyl alcohol into syrupy phosphoric acid heated to about 220° . The phosphoric acid acts as a dehydrating agent.



The reaction is continuous and very large amounts of alcohol can be dehydrated to give ethylene by a relatively small amount of phosphoric acid.

Industrial Preparation. Ethylene can be prepared on a commercial scale by the following methods :

(1) By passing vapour of ethyl alcohol through heated tubes containing alumina or kaolin.



(2) By the controlled hydrogenation of acetylene.

(3) By cracking of petroleum and of lower paraffins present in natural gas.

*Sulphur dioxide is produced by the reduction of sulphuric acid by ethylene and carbon dioxide results from the oxidation of ethyl alcohol by sulphuric acid and ether is formed by the interaction of ethyl hydrogen sulphate and alcohol.

Physical Properties. Ethylene is a colourless gas having a faint ethereal (sweet) odour. It is slightly soluble in organic solvents such as ether and alcohol. Ethylene, when inhaled, produces senselessness and hence it is used as a general anaesthetic.

Chemical Properties As already discussed, ethylene is an unsaturated compound, unstable and highly reactive. The important reactions of ethylene are :

I. Addition Reactions. (i) **Addition of hydrogen.** In the presence of *platinum or palladium catalysts at 90°* and in the presence of *finely divided nickel catalyst at 200°*, ethylene adds one hydrogen molecule to give ethane.



(ii) **Addition of halogens.** Ethylene readily adds chlorine or bromine at ordinary temperatures forming dihalogen derivatives.



The reaction can be carried out by shaking ethylene with a solution of bromine in water or in an organic solvent. The red colour of bromine gets discharged due to the formation of ethylene dibromide which is colourless. The reaction serves as a test for unsaturation.

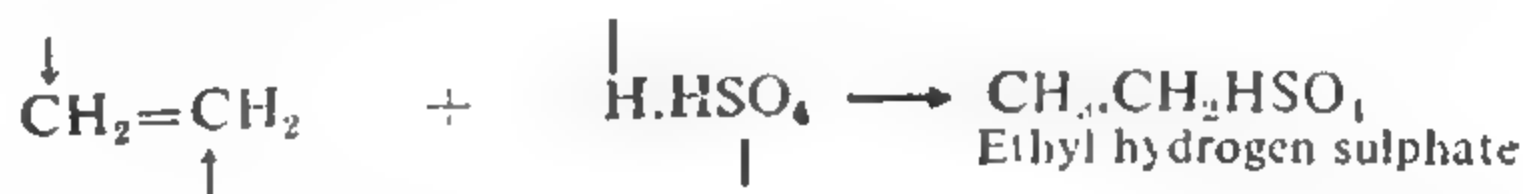
Iodine adds on very slowly. Thus, the *order of reactivity* of halogens is $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

(iii) **Addition of hydrogen halides.** Ethylene readily adds on hydrogen halides (HCl, HBr and HI) forming alkyl halides.



The order of the reactivity of the halides is the reverse of that of the corresponding halogens. It is $\text{HI} > \text{HBr} > \text{HCl}$.

(iv) **Addition of sulphuric acid.** Ethylene is readily absorbed by concentrated sulphuric acid forming ethyl sulphuric acid (ethyl hydrogen sulphate). The reaction involves the addition of sulphuric acid as shown below :



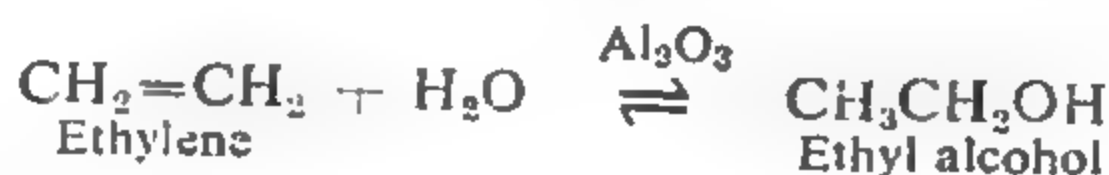
The ethyl hydrogen sulphate is easily hydrolysed by boiling water to give ethyl alcohol.



Thus, ethylene can be easily converted into ethyl alcohol. Large quantities of ethyl alcohol are now-a-days prepared from ethylene (available from coke oven gas or produced by cracking of mineral oils) by this method.

Since the alkanes are not absorbed by sulphuric acid while the alkenes are, the reaction places at our disposal a convenient method of *separating alkanes (paraffins) from alkenes (olefins)*.

(v) **Addition of water.** Ethylene directly combines with water in the presence of *catalysts*, such as *aluminium oxide*, to form an addition product, yielding ethyl alcohol, at *low temperatures* and *high pressures*.



During recent years, this process has gained a good deal of popularity in the U.S.A. for the manufacture of ethyl alcohol from ethylene.

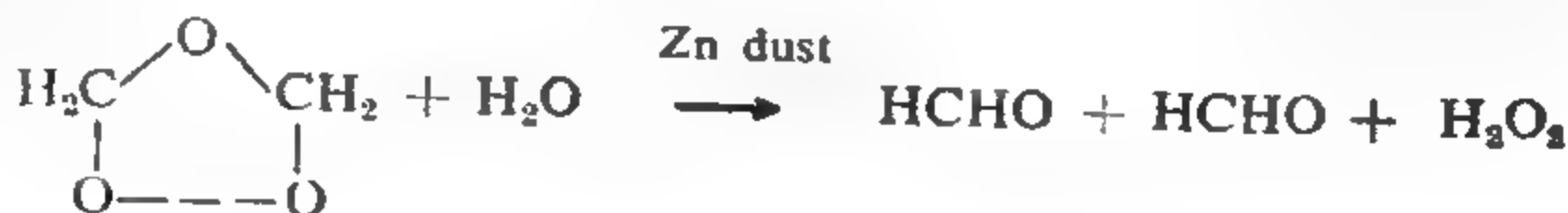
(vi) **Addition of hypochlorous acid.** Ethylene takes up hypochlorous acid from aqueous solution forming ethylene chlorohydrin.



(vii) **Addition of ozone.** When ozonised oxygen is passed through a solution of ethylene in some inert solvent (*i.e.*, a solvent which is not attacked by ozone, such as carbon tetrachloride, ethyl bromide, etc.) at low temperatures, ozone adds across the double bond forming ethylene ozonide.

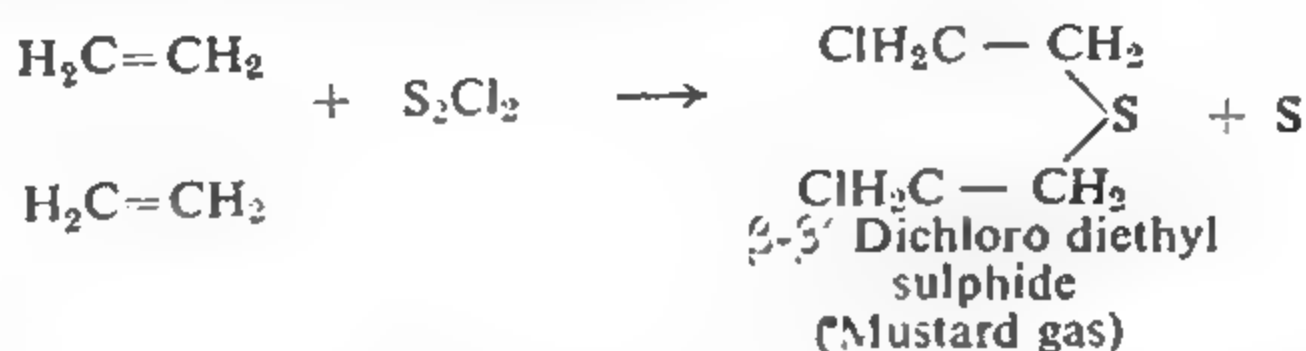


The ozonide can be hydrolysed in the presence of zinc dust to yield an aldehyde



The process of formation of an ozonide by the addition of ozone to an olefin, followed by the hydrolysis of the ozonide is known as **ozonolysis**. The process places at our disposal a valuable method for locating the position of double bond in an olefinic compound.

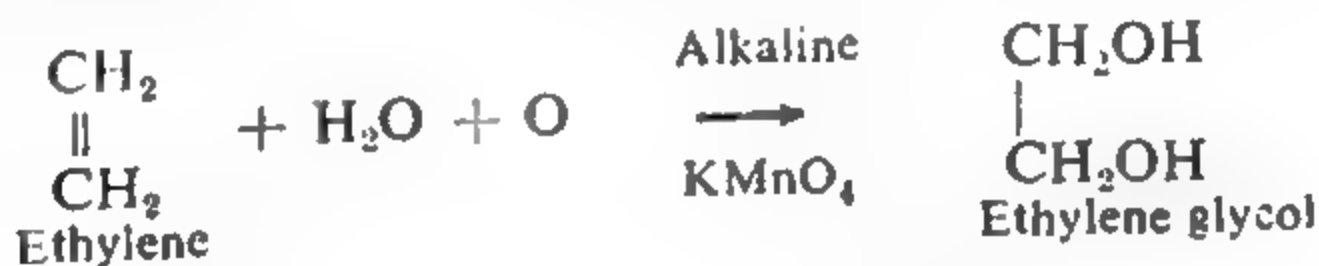
(viii) A special addition reaction of ethylene is the formation of 'mustard gas' by interaction with sulphur monochloride.



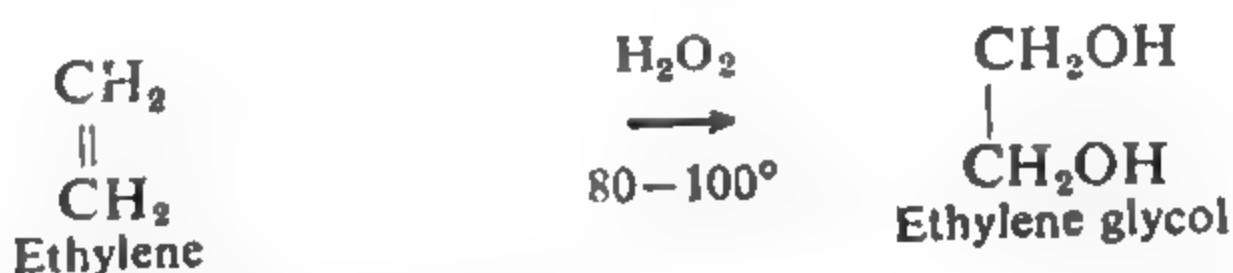
Mustard gas is highly poisonous and is fatal even in very small concentrations.

II. Oxidation Reactions. Because of the presence of a double bond, ethylene is very readily attacked by oxidising agents giving different products under different conditions of oxidation. For example,

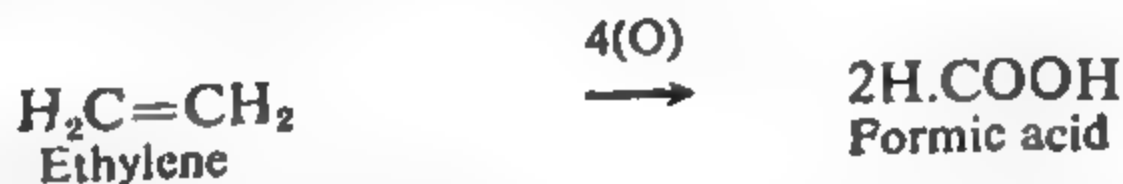
(i) *With alkaline potassium permanganate.* Using 1 per cent aqueous solution of potassium permanganate made alkaline with sodium carbonate, ethylene gives ethylene glycol. The process involves the addition of two (OH) groups which are derived from a molecule of water and an oxygen atom supplied by the permanganate.*



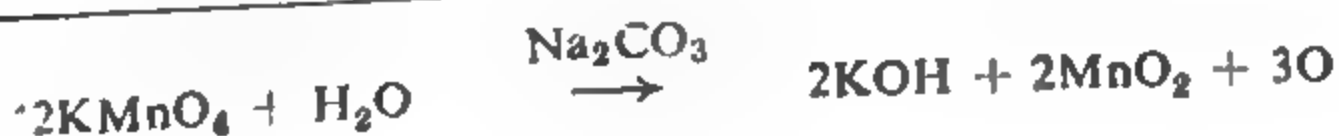
(ii) *With hydrogen peroxide.* On warming ethylene in acetic acid solution with hydrogen peroxide, the end product again is ethylene glycol.



(iii) *With other oxidising agents.* With an excess of a warm concentrated alkaline solution of potassium permanganate or with acidified potassium permanganate or dichromate, ethylene gives formic acid.



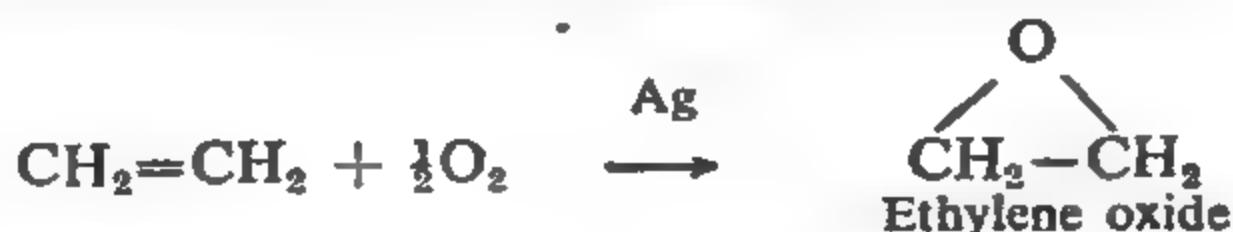
(iv) *Combustion.* When burnt in air or when treated with concentrated nitric acid, ethylene is completely oxidised to carbon dioxide and water.



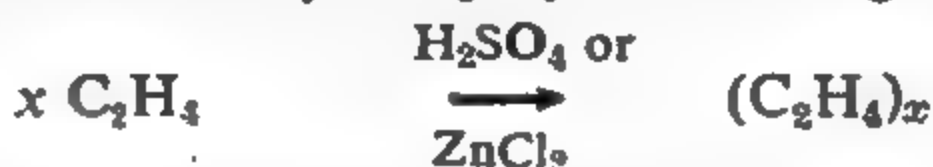
(v) Willstatter and Bommer got formaldehyde by *air-oxidation* of ethylene.



(vi) Ethylene is oxidised to ethylene oxide, when ethylene and air mixture is passed over Ag catalyst heated to about 400° .



III. Polymerisation. In the *presence of sulphuric acid or zinc chloride* and at *high temperatures* ethylene polymerises to give higher olefins.



Thus, liquid hydrocarbons of formulae $\text{C}_{10}\text{H}_{20}$, $\text{C}_{15}\text{H}_{30}$, etc., are easily obtained from ethylene by polymerisation.

Similarly, *liquid ethylene*, when heated with a small proportion of oxygen (catalyst) at $200-400^\circ$ under a high pressure of 1000–1200 atmospheres, yields a high polymer known as **polyethylene**.



Detection of Ethylenic Linkage. The presence of an ethylenic linkage, that is, a double bond, in a molecule can be detected by the following tests :

(1) **Baeyer's Test.** The compound is shaken with 1 per cent aqueous solution of potassium permanganate made alkaline by adding sodium carbonate (*Baeyer's Reagent*). The violet colour of the reagent disappears rapidly

(2) **Addition of bromine.** The compound is well shaken with a 5 per cent solution of bromine in carbon tetrachloride. The red colour of bromine is discharged.

It is important to note, however, that

(i) Both the above tests are also given by compounds containing a triple bond and hence these tests can best be called as **tests for unsaturation**.

(ii) The tests are not applicable to the compounds containing a group or groups having reducing properties.

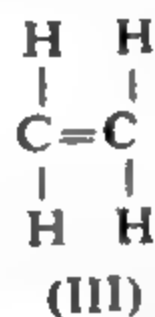
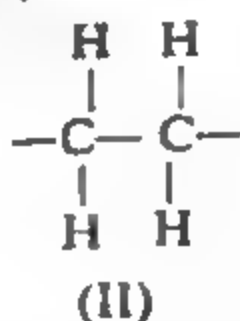
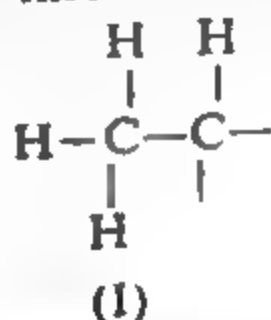
Uses. Ethylene is put to a variety of uses as shown below :

(1) Large amounts of *alcohol* are now produced in U.S.A. by the catalytic hydration of ethylene. (2) *Oxy-ethylene flame* is now replacing the oxy-acetylene flame (for welding purposes) because of the safer transportation of ethylene. (3) Large quantities of the gas are used in, the manufacture of *polyethylene* which is finding extensive use as an insulator and also for the preparation of some laboratory ware, etc.

(4) Ethylene is finding immense use in the *preservation* and *artificial ripening of green fruits* like oranges, apples, banana, etc. In the presence of ethylene (1 part in 1000 parts of air) green fruits ripen and develop their natural colour very rapidly. (5) In recent years, ethylene has replaced ether as an *anaesthetic*. (6) Ethylene is also used for the preparation of *mustard gas* in warfare.

Structure of Ethylene. (1) The analytical data show that the molecular formula of ethylene is C_2H_4 .

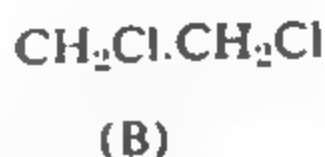
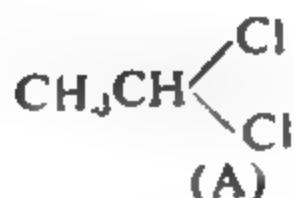
(2) The two atoms of carbon must be linked directly because the union through a monovalent hydrogen atom is not possible. Assuming tetravalency of carbon, the following three structures are possible :



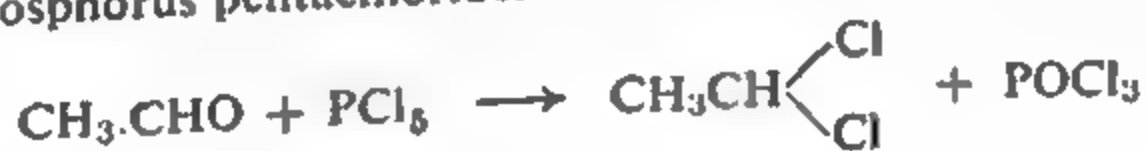
(3) Ethylene combines with chlorine forming ethylene dichloride, $C_2H_4Cl_2$. The two possible structures for $C_2H_4Cl_2$ will evidently be,



i.e.,

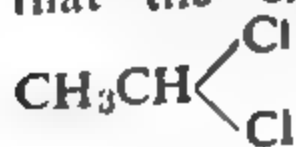


(4) The compound with structure (A) can be obtained from acetaldehyde by the action of phosphorus pentachloride.



This compound boils at 58° .

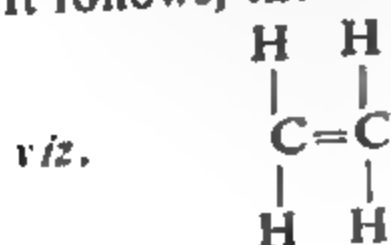
But the compound, $C_2H_4Cl_2$, obtained from ethylene boils at 84° . This shows that the chloride obtained from ethylene cannot have the structure A viz.,



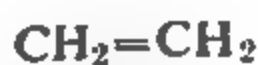
It follows, therefore, that ethylene cannot have the structure I.

(5) According to structure (II), ethylene possesses two "free" bonds which enable it to form addition products. If this is the structure, then a compound, such as $\text{CH}_2\text{Cl}.\text{CH}_2-$, should be possible on the assumption that the two 'free valencies' can exist independently of each other and can be satisfied one at a time. But no such compound is known. The treatment of ethylene with chlorine always gives a dihalogen derivative $C_2H_4Cl_2$. This rules out structure II.

It follows, therefore, that ethylene has the structure III,

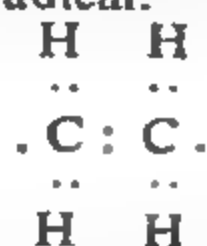


or



(6) The formation of ethylene by the action of zinc on ethylene dibromide (cf. preparation of ethylene) lends further support to the above structure.

(7) *Electronic considerations.* In structure (I) and (II) each 'free' bond stands for *one* electron. In structure (II) if the two electrons are *unpaired* as shown below, it would represent a di-radical.



But ethylene does not give the usual reactions of a di-radical. Hence structure (II) is rejected.

The structure III which is accepted can be represented electronically as :



The space model of ethylene is represented in Fig. 2.

Significance of double bond. The significance of double bond and its stability have been discussed in details in chapter XXIII

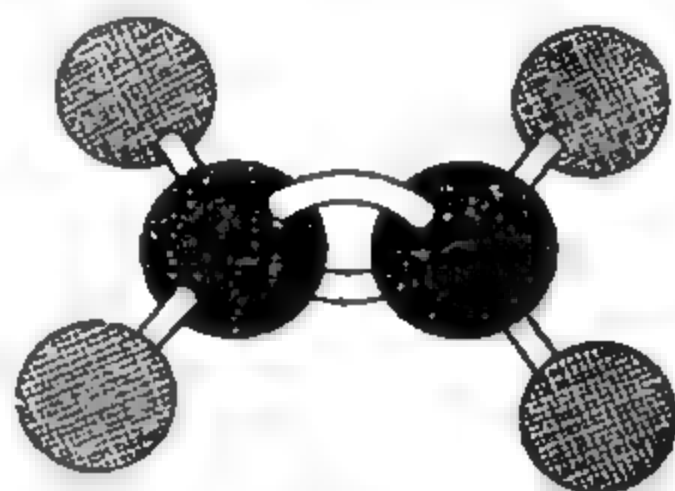


Fig. 2. Space Model of Ethylene

SUMMARY OF A TYPICAL MEMBER

Preparation.

1,2 Dibromo ethane $\text{C}_2\text{H}_4\text{Br}_2$	Distil with zinc	→	
Acetylene $\text{CH}\equiv\text{CH}$	Controlled reduction H_2 (Ni, 200°)	→	
Ethyl alcohol $\text{C}_2\text{H}_5\text{OH}$	Heat with conc. H_2SO_4 170°	→	
Ethyl iodide $\text{C}_2\text{H}_5\text{I}$	Warm with KOH alcoholic	→	→
Ethyl alcohol $\text{C}_2\text{H}_5\text{OH}$	Dehydration with (i) H_3PO_4 (ii) Al_2O_3 at 200°	→	
Pot. succinate $\text{KOOC}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOK}$	Electrolysis	→	
Petroleum	By cracking	→	
			Ethylene $\text{CH}_2=\text{CH}_2$

Properties

Ethylene $\text{CH}_2=\text{CH}_2$	→	Addition of hydrogen $\text{Ni}, 180^\circ$	Ethane C_2H_6
		Addition of halogen, X_2 ($\text{Cl}_2, \text{Br}_2, \text{I}_2$)	Ethylene dihalide $\text{C}_2\text{H}_4\text{X}_2$
		Addition of halogen acid $\text{HX}(\text{HCl}, \text{HBr}, \text{HI})$	Ethyl halide $\text{C}_2\text{H}_5\text{X}$
		Addition of hypochlorous acid (HOCl)	Ethylene Chlorohydrin $\text{CH}_2\text{OHCH}_2\text{Cl}$
		Catalytic addition of H_2O (Al_2O_3)	Ethyl alcohol $\text{C}_2\text{H}_5\text{OH}$
			↓ Hydrolysis
		Treat with equivalent amount of H_2SO_4	Ethyl sulphuric acid $\text{C}_2\text{H}_5\text{HSO}_4$
		Ozone	Ethylene ozonide $\text{C}_2\text{H}_4\text{O}_3$
		Oxidation with dilute alkaline KMnO_4	Glycol $\text{CH}_2\text{OH} \cdot \text{CH}_2\text{OH}$
		Oxidation with acidic KMnO_4	Formic acid HCOOH
		Combustion	$\text{CO}_2 + \text{H}_2\text{O}$
		Polymerisation	Polyethylene
		Oxidation with air Ag coil, 400°	Ethylene oxide CH_2-CH_2 $\diagup \text{O} \diagdown$
		Air Oxidation	Formaldehyde $\text{H} \cdot \text{CHO}$

QUESTIONS

1. What are unsaturated hydrocarbons ? Give some examples and typical reactions to show that they are unsaturated.
2. How is ethylene prepared in the laboratory ? Describe its properties.
3. How can ethylene be prepared in the laboratory ? How can it be converted into (i) Ethane (ii) Ethyl bromide (iii) Ethyl alcohol (iv) Glycol (v) Formic acid.
4. Describe the general methods for the preparation of olefins. What products are obtained when ethylene reacts with (i) bromine (ii) alkaline potassium permanganate (iii) sulphuric acid (iv) ozone (v) hypochlorous acid.
5. How would you establish the structure of ethylene ? What is the significance of a double bond ? Describe briefly the important uses of ethylene.
6. Write short notes on :
 - (i) Addition Reactions
 - (ii) Polymerisation
 - (iii) Markownikoff's rule
7. Give any four general methods of preparation of olefins. (Panjab Inter 1959)
8. Give the important reactions of alkenes or olefins. Explain why are they so reactive. (Panjab Inter 1955 Suppl.)
- Describe any two methods for the preparation of ethylene. How does ethylene react with (i) bromine (ii) hydrobromic acid (iii) concentrated sulphuric acid (iv) ozone ? Give some important uses of ethylene. (Panjab Inter 1949)
10. What evidence have you to prove the structure of ethylene ? Compare and contrast the properties of ethane with those of ethylene ? (Panjab Inter 1943)
11. How are hydrocarbons classified ? Describe the preparation of ethylene in the laboratory. Give equations illustrating the additive reactions of ethylene. (J. & K Inter 1964)
12. Give a sketch of the apparatus used in preparing ethylene. Describe the properties of ethylene. (U. P. Board Inter 1949)
13. How is ethylene prepared ? Give its important reactions. How is its reactivity explained ? (Delhi Pre-medical 1946)
14. Give the preparation of ethylene ? (Rajputana Inter 1952)
15. Describe with practical details the preparation of ethylene in the laboratory. How does it react with (a) bromine, (b) KMnO_4 , (c) ozone ? (Bihar Inter 1956)
16. Fill in the blanks :
 - (i) The presence of a ——— is indicated by decolorisation of ——— water.
 - (ii) Markownikoff's rule governs the addition of ——— to an ——— molecule.
 - (iii) Oxidation of ethylene with Baeyer's reagent yields ———
 - (iv) ——— bond compounds are highly ——— (why) ?
 - (v) Addition of ozone to ethylene yields ———
 - (vi) Dehydration of alcohols with phosphoric acid yield ———
 - (vii) Ethylene polymerises to ——— in the presence of ——— high pressure.
 - (viii) An alkyl halide loses molecule of ——— with alcoholic ——— to yield an olefin

CHAPTER XXVII

ALKYNES OR ACETYLENES

Alkynes. Alknes are those hydrocarbons which contain four hydrogen atoms less than the corresponding paraffins and two hydrogen atoms less than the corresponding olefins. They are also known as **acetylenes** after the name of the first member, **acetylene**.

Each member of the series contains one triple bond in the molecule. For example,

Ethyne or acetylene, C_2H_2 or $HC \equiv CH$

Propyne or methyl acetylene, C_3H_4 or $CH \equiv C \cdot CH_3$

The general formula of the series is C_nH_{2n-2} .

Nomenclature. Acetylenic hydrocarbons or alkynes are named either on the I.U.C. system or as derivatives of acetylene. In the I.U.C. system, their name is obtained by converting the suffix, *-ane* of the corresponding alkane by *yne*. The position of the triple bond is indicated by prefixing the number of the carbon atom preceding it. Thus, we have

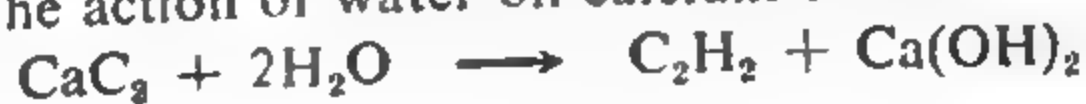
<i>Formula of the alkyne</i>	<i>Common name</i>	<i>I U.C. name.</i>
$HC \equiv CH$	Acetylene	Ethyne
$CH_3 \cdot C \equiv CH$	Methyl-acetylene	Propyne
$CH_3 \cdot C \equiv C \cdot CH_3$	Dimethyl acetylene	2-Butyne
$C_2H_5 \cdot C \equiv CH$	Ethylacetylene	1-Butyne

ACETYLENE, or ETHYNE, C_2H_2 , $CH \equiv CH$

Acetylene is the first and the most important member of the alkyne series. It occurs in coal gas in small amounts (0.06 per cent). It is formed during the incomplete combustion of coal gas, oil gas, ethyl alcohol, hydrocarbons, etc. Thus, when a Bunsen burner strikes back, the issuing gases contain about 1 per cent of acetylene.

Preparation. Acetylene may be prepared by the following methods :

(1) **Laboratory method.** Acetylene is conveniently prepared in the laboratory by the action of water on calcium carbide.



The apparatus used is shown in Fig. 1.

The bottom of the filtration flask is covered by a layer of sand and small lumps of calcium carbide are then added. Water is added *dropwise* through the dropping funnel and the gas is collected over water.

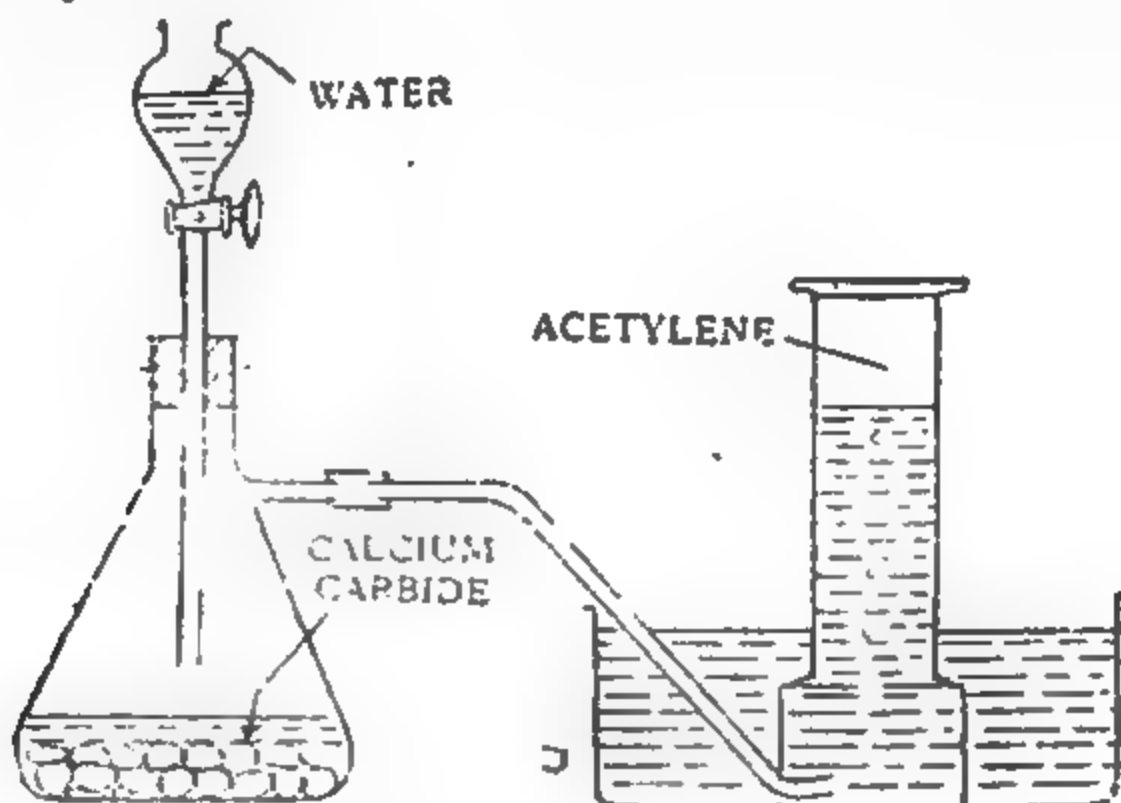


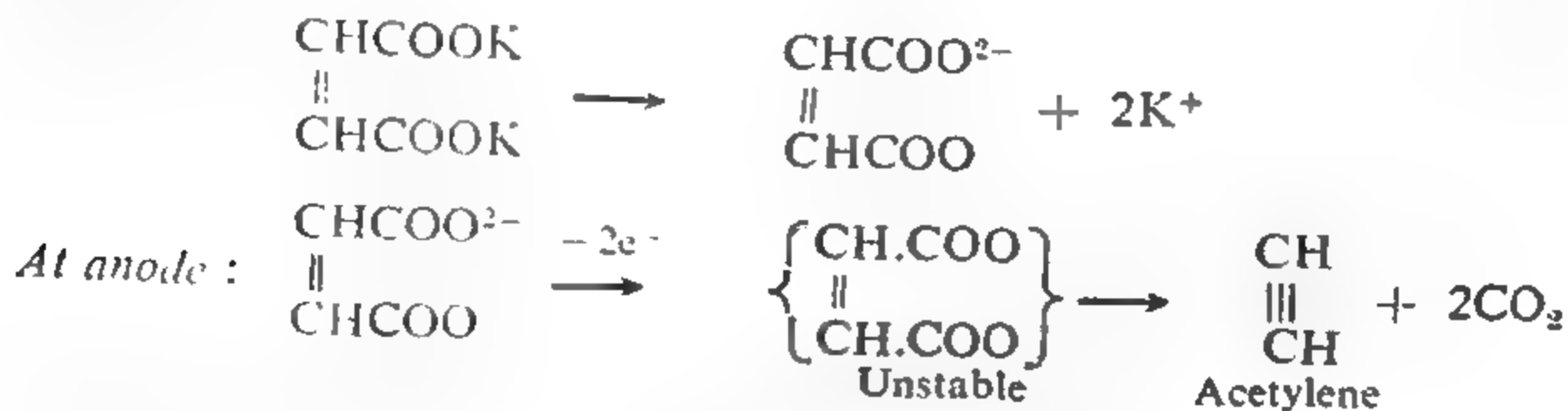
Fig. 1. Preparation of Acetylene

The acetylene obtained is not pure but contains small amounts of phosphine, arsine, hydrogen sulphide, ammonia, etc., depending upon the impurities present in calcium carbide. Acetylene can be freed from these impurities by passing it through an *acidic* solution of copper sulphate which will retain all impurities excepting phosphine. The latter is removed by passing through a suspension of bleaching powder when the phosphine gets oxidised to phosphoric acid which is retained by the suspension.

(2) By heating a trihalogen derivative of methane with silver powder. Iodoform when heated with silver powder yields acetylene.

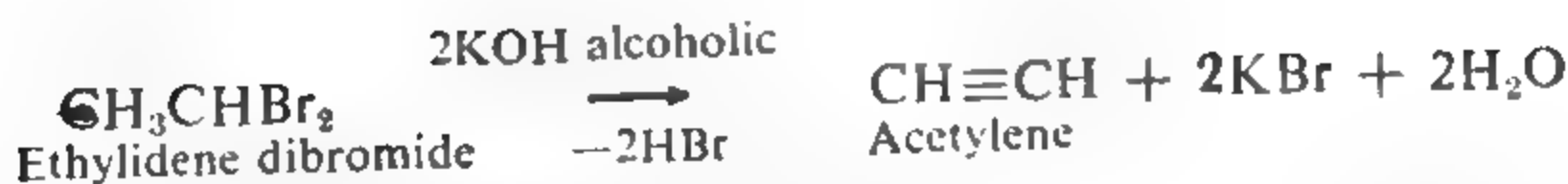


(3) By the electrolysis of an aqueous solution of sodium (or potassium) fumarate or maleate.



(4) By the action of alcoholic potash on ethylene dibromide or ethylidene dibromide.





(5) **Synthesis.** Acetylene was first synthesised by Berthelot in 1859 by passing an electric arc between carbon electrodes in a current of hydrogen.



(6) **Industrial preparation.** (i) Since calcium carbide can be readily manufactured by heating calcium oxide with coke in an electric furnace,



acetylene, on an industrial scale also, is obtained by the action of water on calcium carbide. A diagrammatic sketch of the plant used for the purpose is shown in Fig. 2.

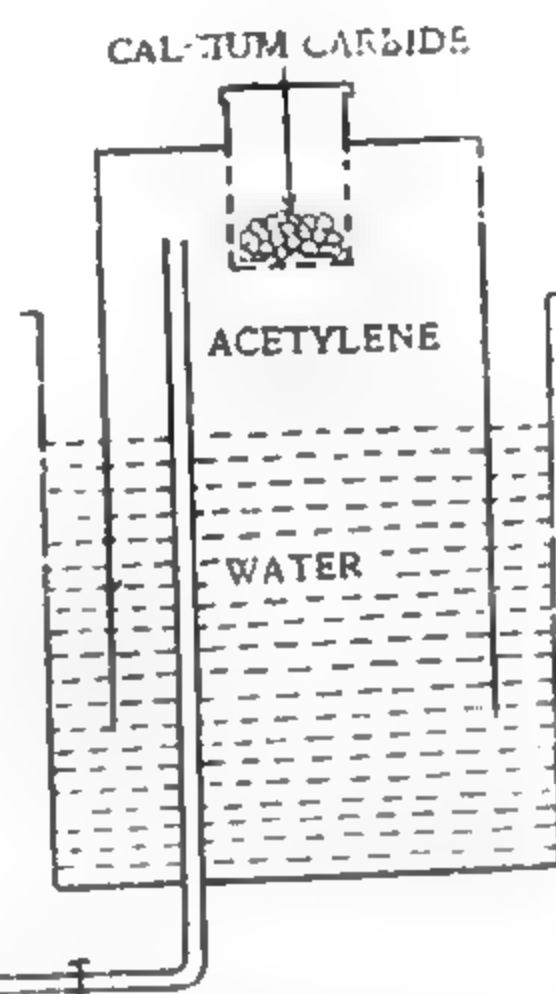


Fig. 2. Manufacture of acetylene

(ii) A more recent method for the industrial preparation of acetylene involves the *cracking of methane-ethane mixtures by an electric arc*. The yield is about 45 per cent.



(iii) Another process used for large scale production of acetylene is by bringing about *partial oxidation of methane at high temperatures*.



Physical Properties. Acetylene is a colourless gas having an ethereal smell when pure. The characteristic garlic odour of acetylene is due to the presence of impurities, particularly phosphine. It is only slightly soluble in water but more so in alcohol and still more in acetone. It is in the form of acetone solution that acetylene is transported when required for welding purposes because *gaseous acetylene is liable to explode violently by mere shock*.

Chemical Properties (1) **Decomposition.** Acetylene is an unstable compound and decomposes into its elements with an explosive violence if the compressed gas is *detonated*.



Carbon obtained above is in a finely divided state and is used as carbon black.

(2) **Combustion** (i) Acetylene is a combustible gas and burns with luminous, smoky flame. When mixed with oxygen it burns with an

intensely hot flame giving a temperature of about 2700° .



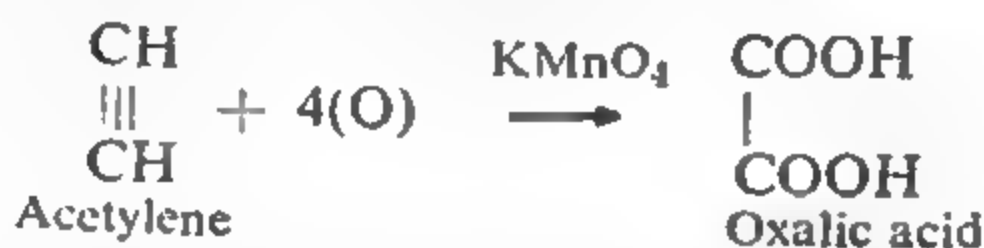
The *oxy-acetylene flame* is one of the hottest flames, and is used for welding, cutting and making holes in steel plates, etc.

Acetylene, like other hydrocarbons, forms *explosive mixtures with air*.

(ii) Acetylene catches fire when brought in contact with *gaseous chlorine*, giving free carbon and hydrochloric acid gas.

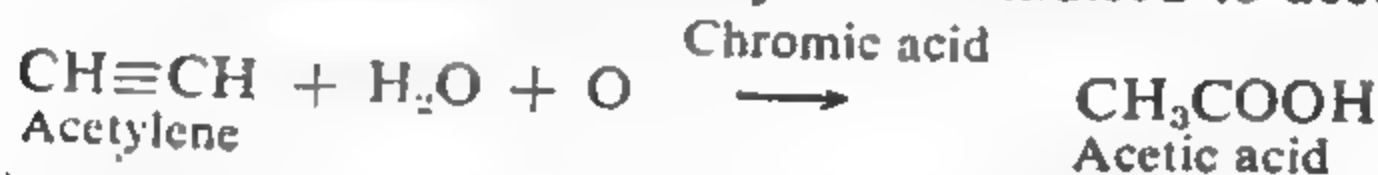


(3) **Oxidation.** (i) With potassium permanganate (acidic or alkaline) acetylene is oxidised to oxalic acid.



Acetylene, thus, decolorises potassium permanganate solution.

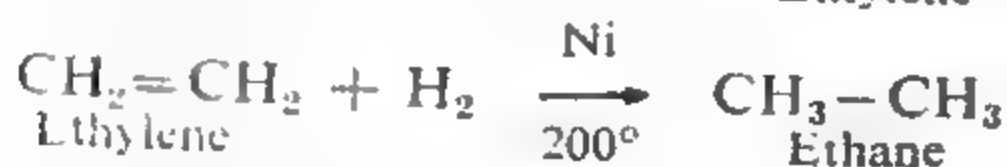
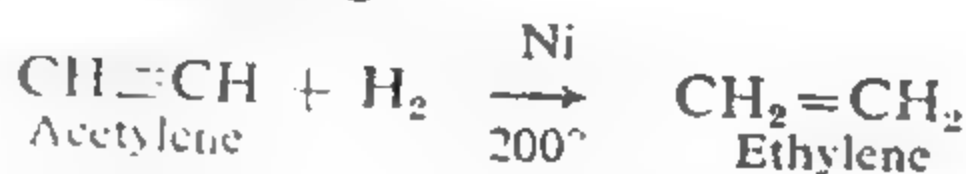
(ii) With *chromic acid*, acetylene is oxidised to acetic acid.



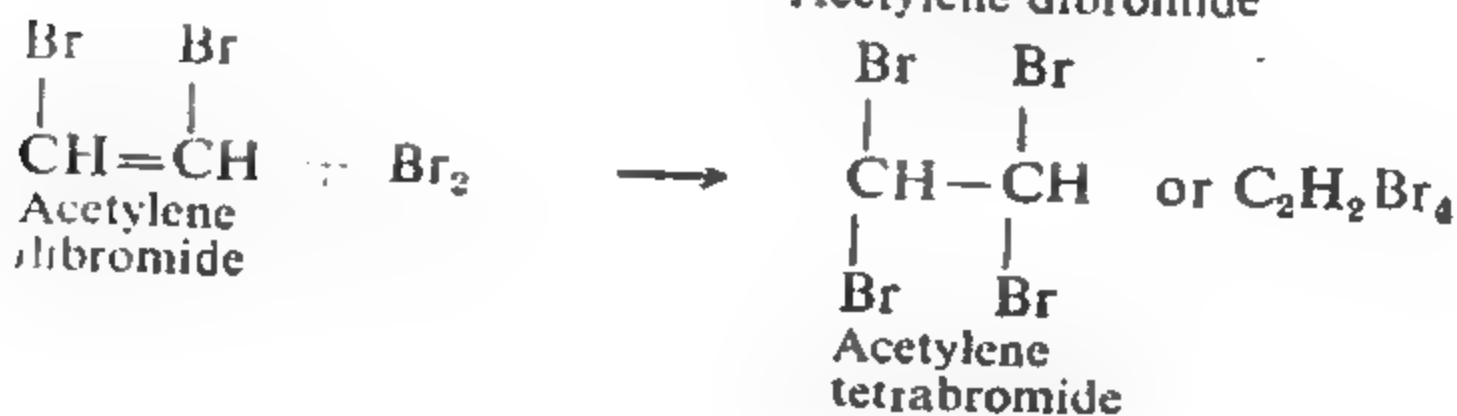
(4) **Addition Reactions.** Since acetylene contains a triple bond which is equivalent to two double bonds, it gives addition reactions in a manner similar to the olefins. The addition capacity of acetylene is twice as much as that of ethylene and hence it enters into addition reactions somewhat more readily than the olefins.

Additions of hydrogen, halogens, and hydrogen halides (halogen acids) take place in two stages, as illustrated below :

(i) **Addition of hydrogen.**

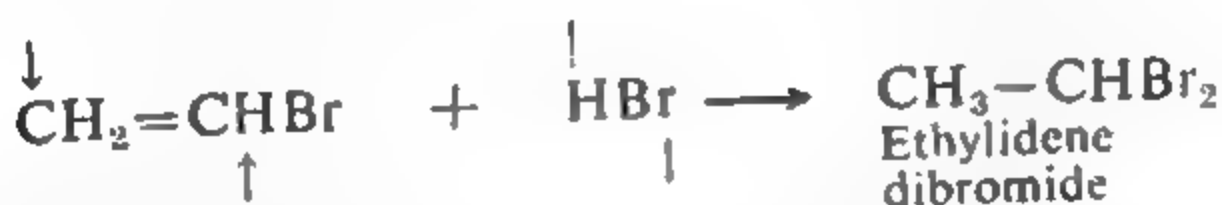


(ii) **Addition of halogens.**



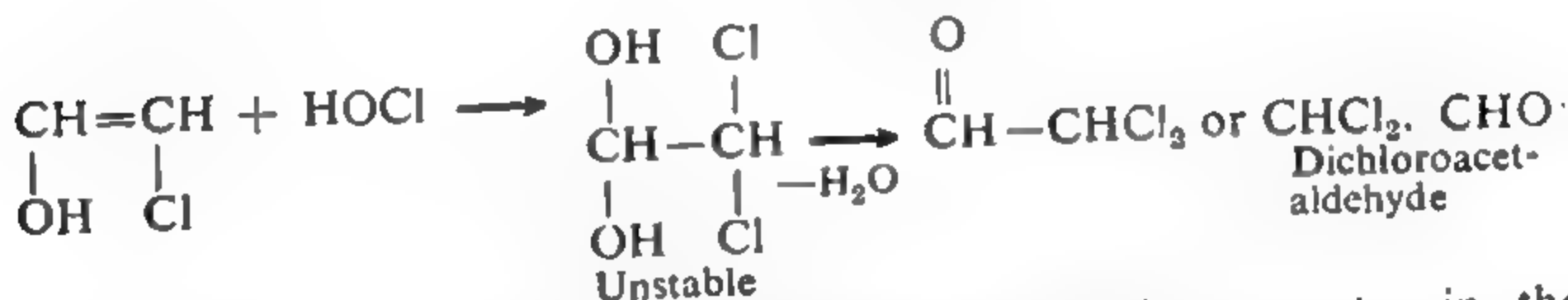
With gaseous chlorine, as already mentioned, acetylene gets ignited, giving carbon and hydrogen chloride gas.

(iii) **Addition of hydrogen halides (halogen acids).** This addition also takes place in two stages, the second stage follows the **Markownikoff's rule**.

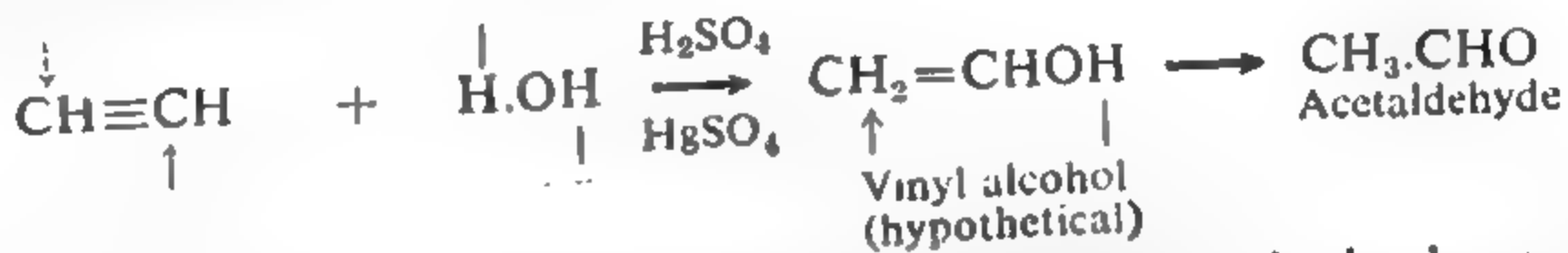


Vinyl bromide
Similar reactions take place with hydrogen chloride and hydrogen iodide.

(iv) Addition of hypochlorous acid. The resulting product in this-

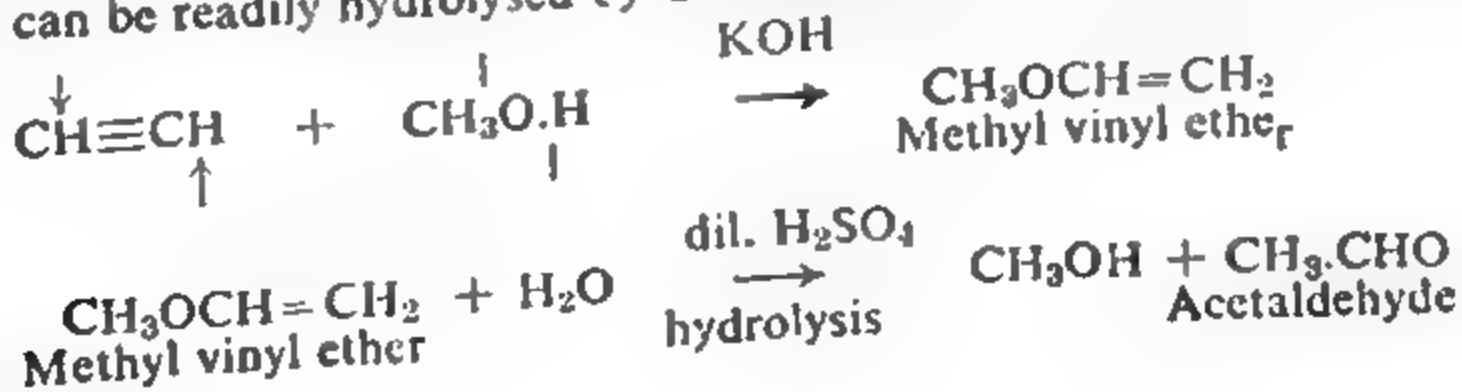


(v) **Addition of water.** Acetylene directly adds on water in the presence of hot dilute sulphuric acid, containing a little mercuric sulphate, giving acetaldehyde.



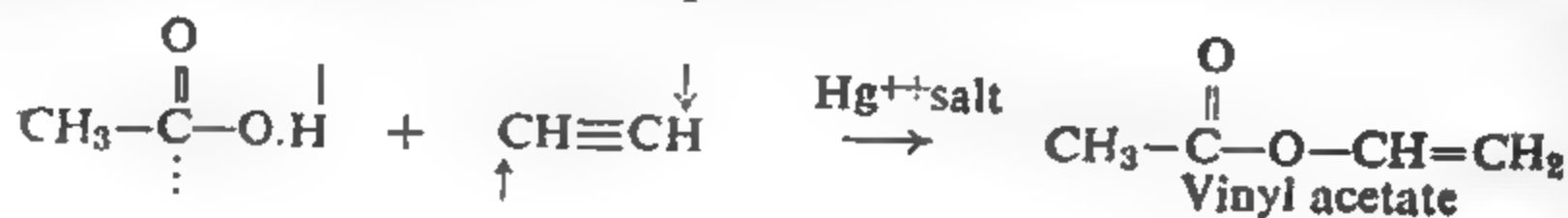
This is a very important reaction as the acetaldehyde obtained can be used for the preparation of ethyl alcohol (by reduction) and acetic acid (by oxidation)

(vi) Addition of methyl alcohol. Like water, methyl alcohol also adds on to acetylene in the presence of 80–95% potassium hydroxide giving methyl vinyl ether which can be readily hydrolysed by dilute sulphuric acid giving acetaldehyde.



The methyl alcohol generated is reused. The reaction thus provides an excellent method for the *conversion of acetylene into acetaldehyde*.

(vii) **Addition of acetic acid.** Acetylene adds on acetic acid in the presence of a catalyst (mercuric salt) to give vinyl acetate which is required for the production of vinyl resins used as *synthetic rubber and plastics*.



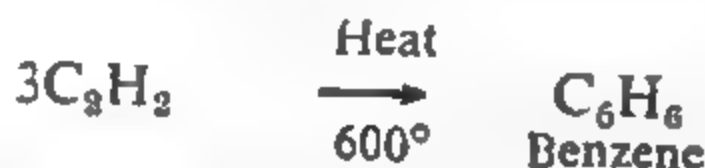
(viii) **Addition of HCN.** Acetylene adds on hydrogen cyanide to yield acrylonitrile, which is an important starting material for synthetic rubber.



(ix) **Addition of ozone** Acetylene, like olefins, adds on ozone giving ozonide.

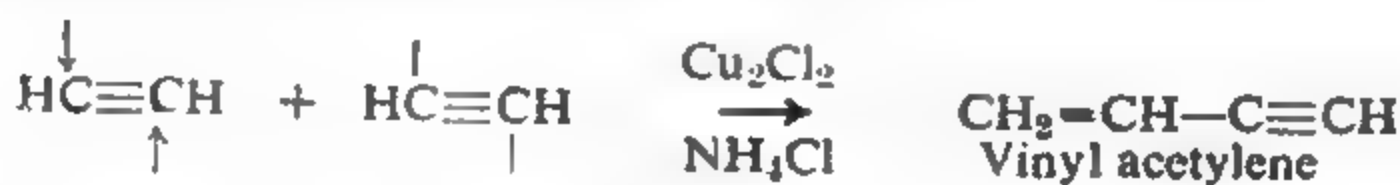


() **Polymerisation.** (i) Acetylene, when heated in a quartz or copper or iron tube to dull red heat, polymerises to give benzene.



This reaction gives us an important method of passing from aliphatic to aromatic compounds.

(ii) Acetylene, when absorbed in a solution of cuprous chloride and ammonium chloride in hydrochloric acid, polymerises to give vinyl acetylene which is used for the manufacture of synthetic rubber.



(6) **Formation of Metallic Derivatives.** A unique characteristic of acetylene is that the hydrogen atom attached to the triple bond carbon atom is acidic in nature and can be replaced by metals.

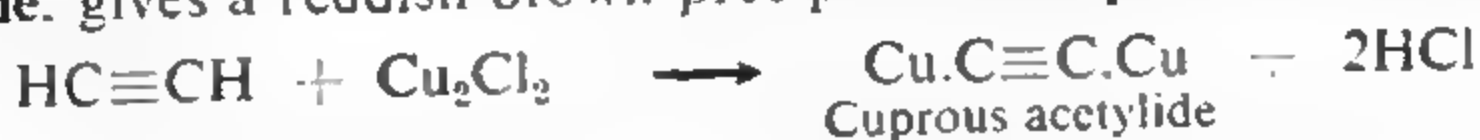
(a) Thus, acetylene when passed into a solution of sodium in liquid ammonia, gives mono-sodium and disodium acetylides.



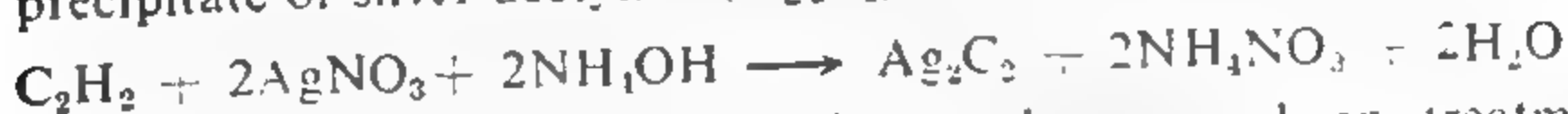
Sodium acetylide can also be obtained by the interaction of acetylene with sodamide.



(b) Acetylene when passed through an ammoniacal solution of cuprous chloride, gives a reddish brown precipitate of cuprous acetylide.



(c) Similarly, with ammoniacal solution of silver nitrate, a white precipitate of silver acetylide (Ag_2C_2) is obtained.



The silver and copper acetylides are decomposed on treatment with dilute mineral acids to give back acetylene.

For example,



The formation of acetylide precipitates is used as a *diagnostic test for acetylene*.

Also since these acetylides readily yield acetylene on treatment with mineral acids, the reaction is utilised for the *purification of acetylene* and for its *separation* from olefins and paraffins.

The copper and silver acetylides are highly explosive in dry state.

Uses. Acetylene is used :

(1) As an *illuminant* in light houses, signal lamps, hawker's lamps, etc. A simple hawker's lamp is diagrammatically shown in Fig. 3.

(2) For producing *oxy-acetylene flame* for welding iron, steel and other metals and for cutting steel plates and bars. Oxygen-acetylene flame gives a temperature of about 2800° . An oxy-acetylene torch used for the above purposes is shown in Fig. 4.

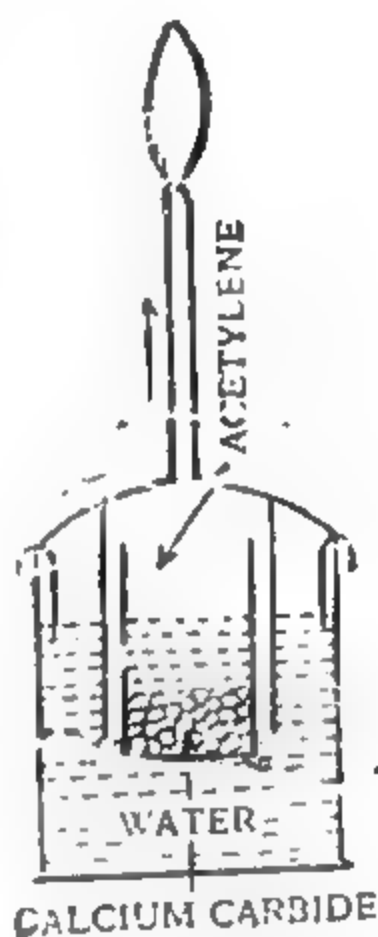


Fig. 3. Hawker's Acetylene Lamp

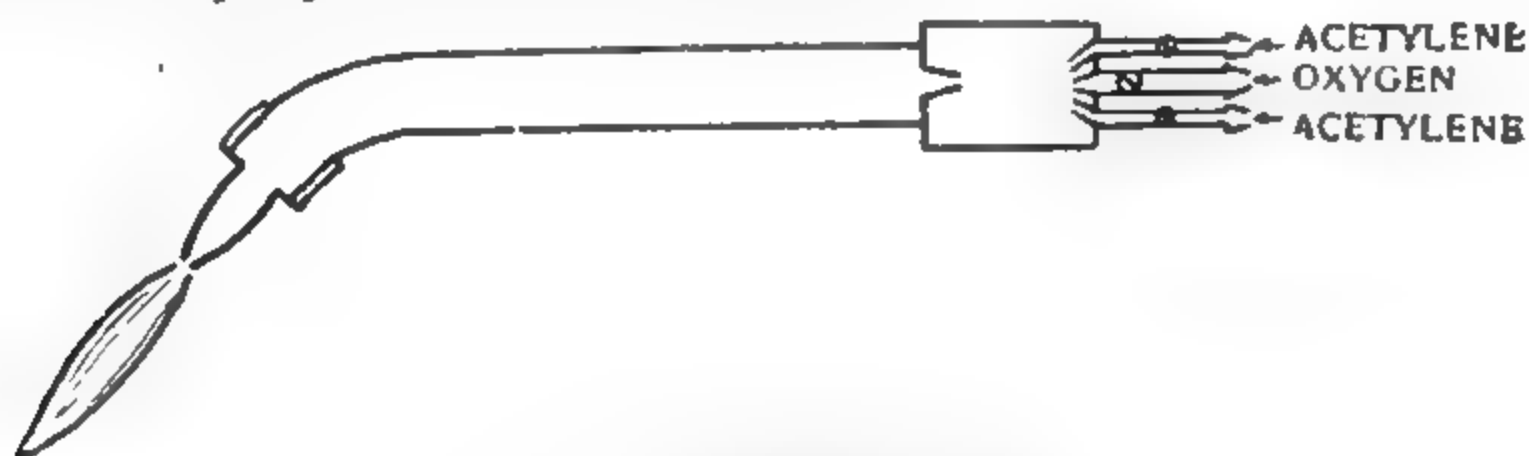


Fig. 4. Oxy-acetylene torch

(3) For the manufacture of hydrogen and lamp black.

(4) As a starting material for the manufacture of a number of organic compounds such as *acetaldehyde*, *ethyl alcohol*, *acetic acid*, *ethyl acetate*, etc.

(5) For the preparation of important products such as *vinyl acetate* for plastics ; *westron* ($C_2H_2Cl_4$) and *westrosol* ($CCl_2=CHCl$) as solvents and *lewisite* ($Cl.CH=CH.AsCl_2$) as a war gas.

(6) For the artificial ripening of fruit and vegetables.

(7) Pure acetylene is also used as an anaesthetic under the name *narcylen*.

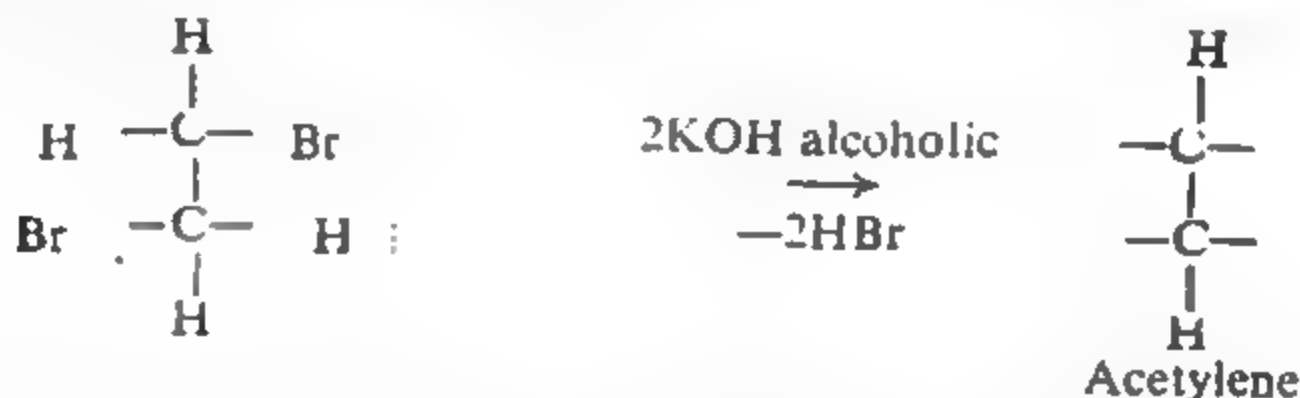
Structure of Acetylene. (1) By gas analysis, the molecular formula of acetylene is found to be C_2H_2 .

(2) The two atoms of carbon must be linked directly because the union through a monovalent hydrogen is not possible. Assuming tetravalency of carbon, the following two structures are possible :



(3) With chlorine, acetylene gives a product having the structure $CHCl_2-CHCl_2$. This rules out formula A.

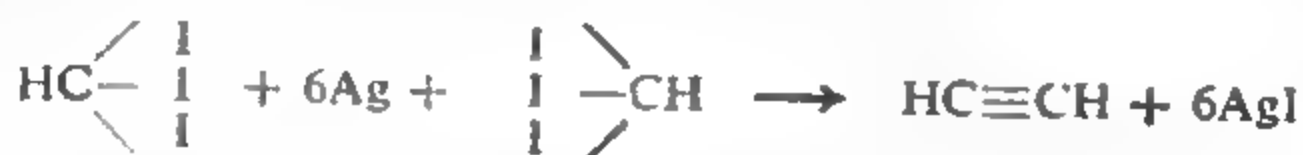
(4) Formula B is supported by the preparation of acetylene from ethylene dibromide by the action of alcoholic potash.



(5) As discussed in the previous chapter (cf. structure of ethylene), 'free' valencies attached to carbon atom cannot exist. Hence the two carbon atoms in acetylene are linked by a triple bond. Acetylene, thus, has the structure



(6) This structure is supported by its synthesis from iodoform by heating with silver powder.



(7) **Electronic formula.** Electronic formula of acetylene is represented below :



8. **Space Model.** The space model of acetylene is shown in Fig. 5.

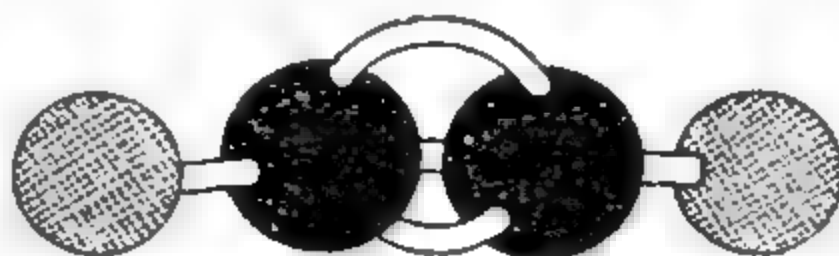
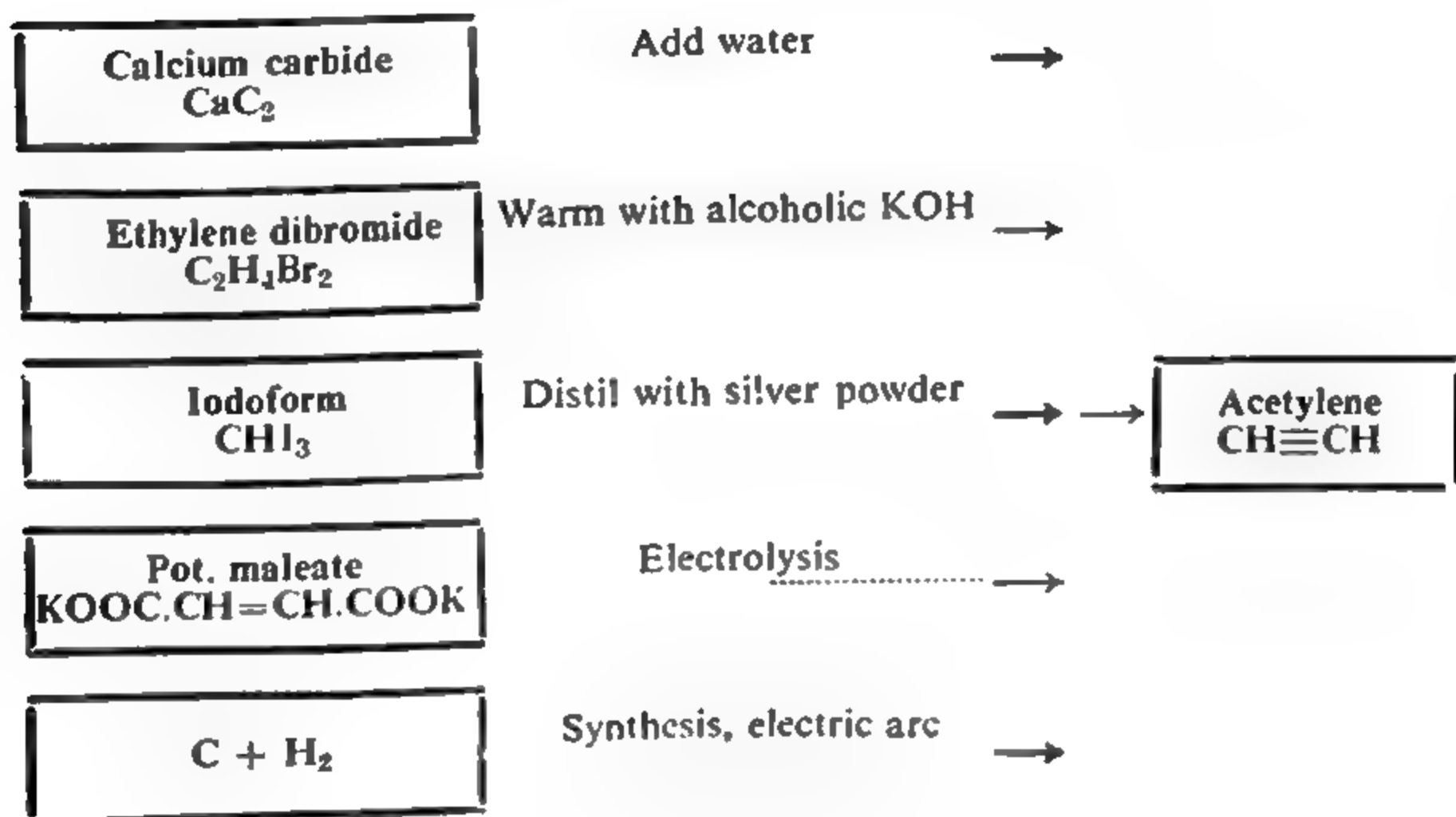


Fig. 5. Space Model of Acetylene

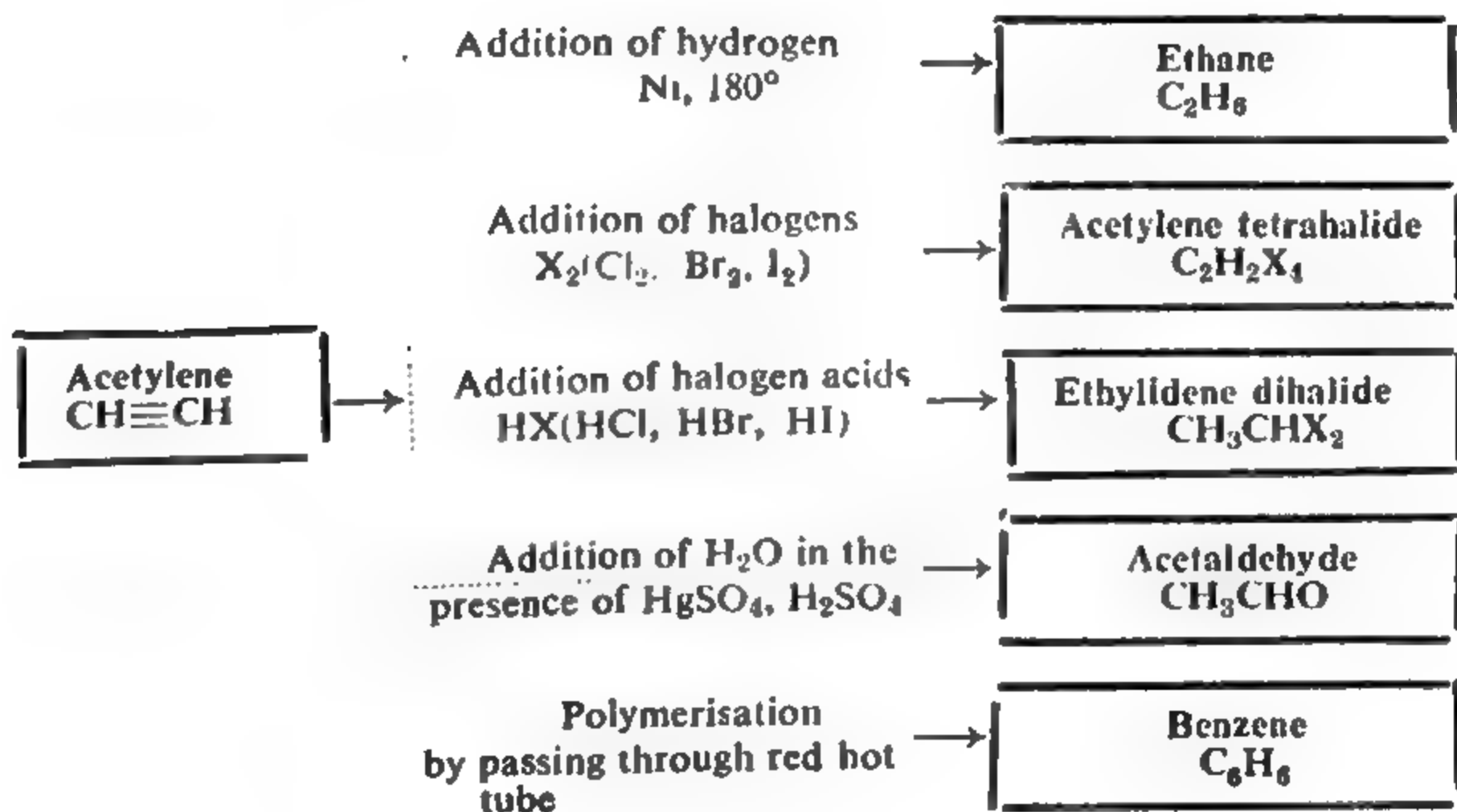
SUMMARY OF A TYPICAL MEMBER

PREPARATION AND PROPERTIES OF ACETYLENE

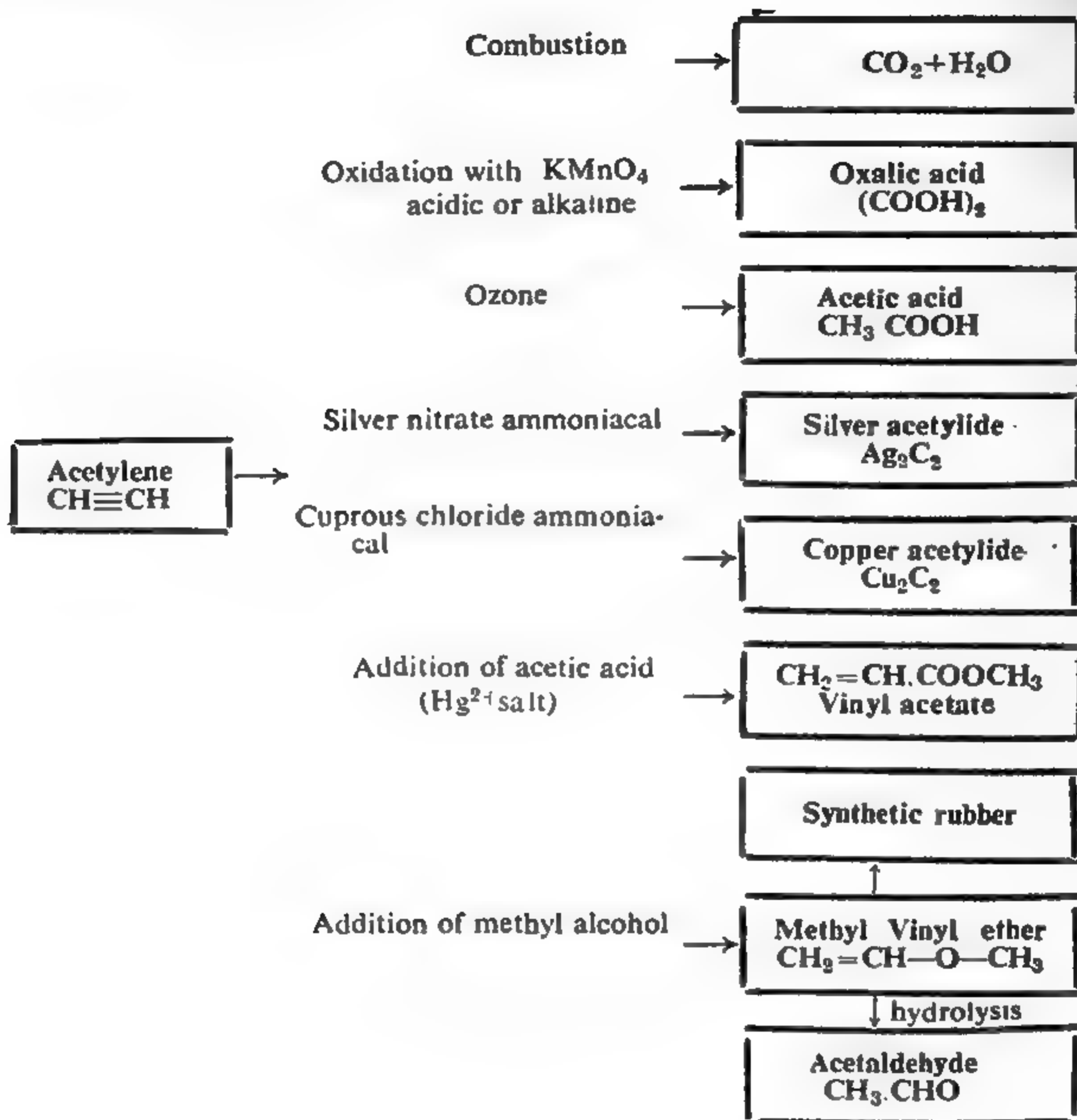
Preparation.



Properties.



Properties (Continued)



QUESTIONS

1. What are alkynes? Give their general formula and the names and structural formulae of the first two members.

2. How is acetylene prepared (i) on a laboratory scale (ii) on a large scale? Give the important properties and uses of acetylene.

3. How is pure acetylene prepared in the laboratory? Explain how can it be converted into (i) Ethylene (ii) Ethane (iii) Acetaldehyde (iv) Acetic Acid (v) Oxalic acid (vi) Benzene (vii) Vinyl acetate (viii) Lewisite?

4. What organic compound is obtained by the action of water on calcium carbide? Give four typical reactions of the compound.

5. How is acetylene prepared? Describe its properties and important uses.

6. How is pure acetylene prepared in the laboratory? How has its structure been established? Give the important uses and tests of acetylene.

7. Acetylene is a hydrocarbon. Can you explain why it forms metallic derivatives? Name *three* such derivatives and draw a self explanatory diagram to show how you can prepare the hydrocarbon from one of them. Mention its industrial uses.
(Panjab Inter 1948)

8. Give the structural formula of the organic compound produced by the action of water on calcium carbide. How is this compound purified? Describe its important properties.

9. How is acetylene prepared in the laboratory? Give its properties and uses.
(Ajmer Inter 1954)

10. By what methods can acetylene be obtained? How may the following substances be made from it:

(a) acetaldehyde (b) acetone (c) isopropyl alcohol? (Panjab Inter 1946)

11. What are acetylene hydrocarbons? How is acetylene prepared? Give its important properties and uses.
(U.P. Inter 1958)

12. How is acetylene prepared? Compare its properties with those of ethane and ethylene.
(Osmania Inter 1955)

13. What are unsaturated hydrocarbons? Show how their reactions differ from those of saturated hydrocarbons.
(Travancore Inter 1956)

14. How is acetylene prepared and what are its properties and uses?
(Madras Inter 1956)

15. Describe the laboratory and large scale methods of preparation of acetylene. Give its properties and uses.
(Panjab, T.D.C. Part I 1962 S)

16. Give laboratory method and purification of acetylene. How can the following substances be obtained from acetylene:

- (a) Acetaldehyde
- (b) Vinyl-chloride
- (c) Silver acetylide
- (d) Benzene

(Panjab T.D.C. Part I 1964)

CHAPTER XXVIII

A COMPARATIVE STUDY OF HYDROCARBONS AND DETERMINATION OF THEIR FORMULAE AND COMPOSITIONS

In the preceding chapters, the three types of hydrocarbons, namely the **paraffins**, the **olefins**, and the **acetylenes**, have been dealt with in details. It is intended to make a comparative study of the hydrocarbons in this chapter as it will afford an opportunity to highlight their *common characteristics, essential differences, interconversions, and separation* from one another.

The methods used in determining their **molecular formulae** will also be discussed.

Physical Properties. The three types of hydrocarbons resemble one another in their physical properties. For example,

(i) The first three or four members of all the three series are gases, the next ten to twelve members are liquids and the higher ones are solids.

(ii) The melting points and boiling points of all the three types of hydrocarbons increase regularly with increase of molecular weights. However, the acetylenes are less volatile than the corresponding paraffins which in turn are less volatile than the olefins. The order of the boiling points is thus

Acetylenes > Paraffins > Olefins.

(iii) The specific gravities also increase regularly with increase in the number of carbon atoms. All hydrocarbons are lighter than water.

(iv) All the three types of hydrocarbons are only slightly soluble in water but dissolve readily in organic solvents such as alcohol, benzene, acetone, etc.

Chemical Properties. While the three types of hydrocarbons are similar in their physical properties, *they differ appreciably in their chemical properties.*

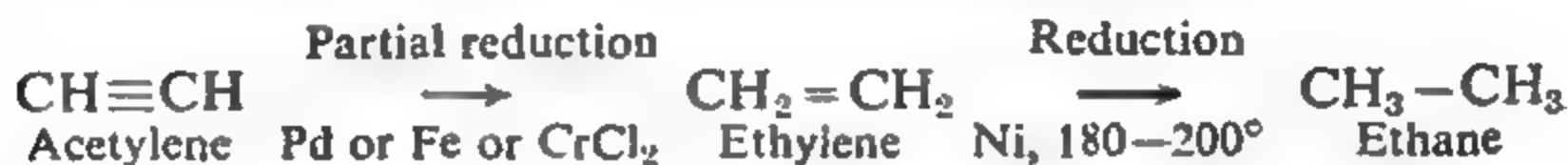
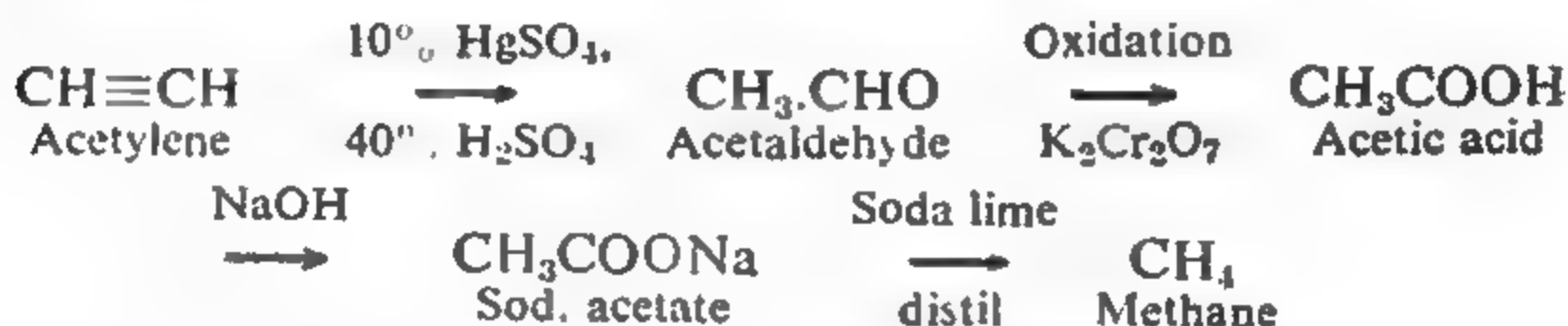
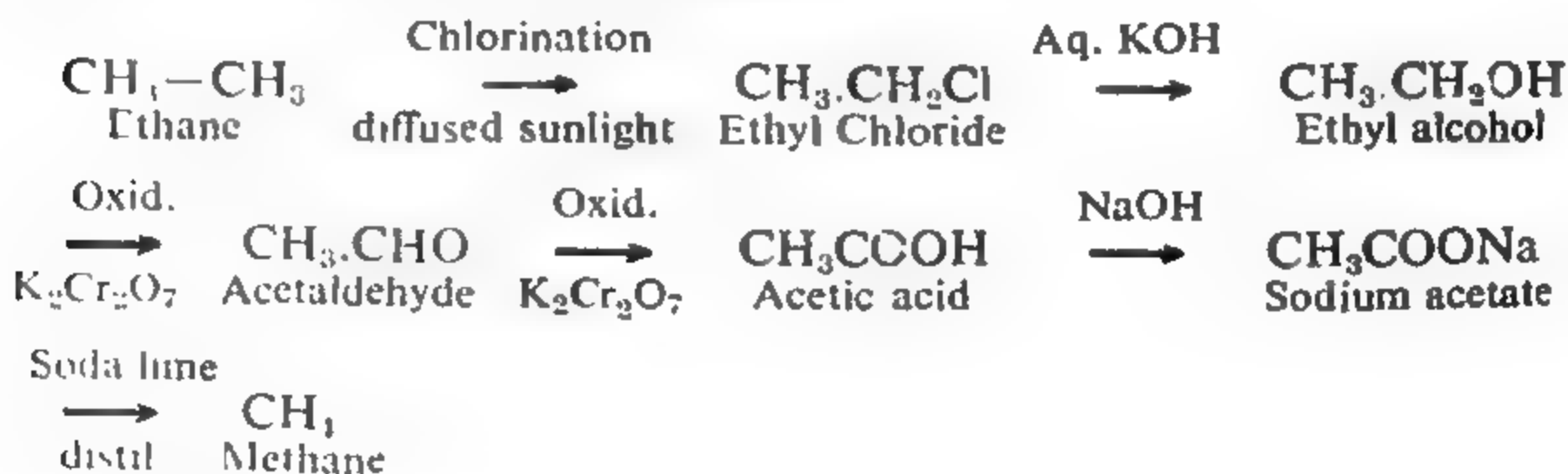
The **paraffins**, since they are *saturated*, are *stable* compounds apparently *inert* and are not *ordinarily* attacked by reagents like nitric acid, sulphuric acid, hydrochloric acid, potassium permanganate, potassium dichromate, etc. On the other hand, the **olefins** and **acetylenes**, being *unsaturated*, are *unstable* and highly *reactive*. They are readily attacked

by reagents like sulphuric acid, nitric acid, hydrochloric acid, potassium permanganate, etc. In their chemical reactivity, the acetylenes surpass even the olefins.

Some of the typical reactions, giving a comparison between the three types of hydrocarbons, are summarised in the following table. *The equations for the various reactions may be looked up in the previous pages.*

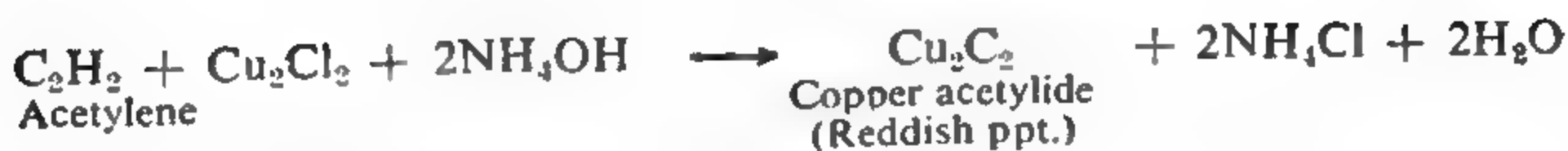
Comparison between Ethane, Ethylene and Acetylene

Chemical Property	Ethane	Ethylene	Acetylene
1. Combustion	Burns with a non-luminous flame.	Burns with a luminous flame.	Burns with a smoky flame.
2. With halogens	Forms substitution products.	Forms addition products, adding two atoms of the halogen at the double bond.	Forms addition products, adding four atoms of the halogen at the triple bond.
3. With halogen acids	No action.	Forms addition products, adding one molecule of the halogen acid at the double bond.	Forms addition products adding two molecules of the halogen acid at the triple bond.
4. With hypohalogen acids	No action.	Forms addition products adding one molecule of the hypohalogen acid at the double bond.	Forms addition products adding two molecules of the hypohalogen acid at the triple bond.
5. With alkaline potassium permanganate	No action.	Forms glycol.	Forms oxalic acid.
6. With ozone	No action.	Forms ozonide.	Forms ozonide.
7. With ammoniacal AgNO_3 or Cu_2Cl_2	No action.	No action.	Forms silver or copper acetylide.
8. Polymerisation	No action.	Polymerises to polyethylene.	Polymerises to benzene and vinyl acetylene.
9. With H_2SO_4	No action.	Forms the addition product, ethyl hydrogen sulphate.	With dil. H_2SO_4 , in the presence of HgSO_4 as a catalyst, acetaldehyde is formed.

Interconversions of Hydrocarbons.**(i) Conversion of ethane into ethylene.****(ii) Conversion of ethylene into Acetylene.****(iii) Conversion of acetylene into ethylene and ethane.****(iv) Conversion of acetylene into methane.****(v) Conversion of methane into ethane.****(vi) Conversion of ethane into methane.****Separation of Hydrocarbons**

A gaseous mixture of paraffins, olefins and acetylenes can be separated into its constituents by suitable means. For example, a mixture of ethane, ethylene and acetylene can be separated as below :

(1) **Separation of acetylene.** The gaseous mixture containing ethane, ethylene and acetylene is treated with an ammoniacal solution of cuprous chloride (or silver nitrate) when acetylene is precipitated as cuprous (or silver) acetylide.



The other two gases remain unattacked.

The copper acetylide is removed and warmed with dilute hydrochloric acid or sulphuric acid to *regenerate* acetylene.



(2) **Separation of ethylene.** The remaining gaseous mixture is then treated with concentrated sulphuric acid when ethylene is absorbed as ethyl hydrogen sulphate.



The ethyl hydrogen sulphate is separated and heated to *set free* ethylene.



(3) The residual gas is **ethane**.

Composition of Gaseous Mixtures

The composition of a gaseous mixture of two hydrocarbons can be determined by noting the volume of oxygen used for the combustion of a known volume of the gaseous mixture. If the mixture contains more than two hydrocarbons, the volume of the carbon dioxide produced during combustion should also be known. This will be clear from the following examples :

Example 1. 30 ml. of a mixture of methane (CH_4) and propane (C_3H_8) required 114 ml. of oxygen for complete combustion. Find out the composition of the mixture.

Total volume of the mixture = 30 ml.

Let the volume of methane = x ml.

Volume of propane = $(30-x)$ ml.

Oxygen used for combustion = 114 ml.

The total volume of oxygen required for the combustion of the mixture can be calculated from the following equations :



Volume of oxygen required for the combustion of x ml. of methane = $2x$ ml.

Volume of oxygen required for the combustion of $(30-x)$ ml. of propane = $5(30-x)$ ml.

$$\therefore \text{Total volume of oxygen required} = 2x + 5(30-x)$$

$$2x + 5(30-x) = 114$$

$$x = 12 \text{ ml.}$$

$$\therefore \text{Volume of methane} = 12 \text{ ml.}$$

$$\text{Volume of propane} = 18 \text{ ml.}$$

Example 2. 25 ml. of a mixture of ethane and ethylene was exploded with 90 ml. of oxygen. The carbon dioxide was absorbed by caustic potash. The remaining gas measuring 10 ml. was absorbed completely by alkaline pyrogallol. Calculate the composition of the mixture.

Total volume of the mixture = 25 ml.

Let the volume of ethane = x ml.

\therefore Volume of ethylene = $(25-x)$ ml.

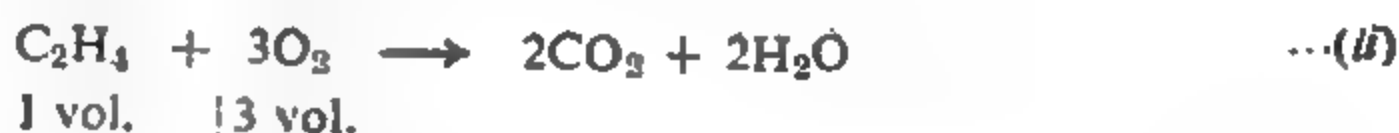
Total volume of oxygen taken = 90 ml.

The volume of unused oxygen = 10 ml.

(which was absorbed by pyrogallol)

\therefore Volume of oxygen used for combustion = $90-10=80$ ml.

The combustion of ethane and ethylene is represented by the following equations :



\therefore Oxygen required for the combustion of

$$x \text{ ml. of ethane} = \frac{7x}{2} \text{ ml. (cf. equation i)}$$

Oxygen required for the combustion of

$$(25-x) \text{ ml. of ethylene} = 3(25-x) \text{ ml. (cf. equation ii)}$$

$$\therefore \text{Total oxygen required} = \frac{7x}{2} + 3(25-x)$$

$$\therefore \frac{7x}{2} + 3(25-x) = 80$$

$$\text{or } x = 10$$

\therefore Volume of ethane = 10 ml.
and Volume of ethylene = 15 ml..

Example 3. 45 ml. of a mixture of methane, ethylene and acetylene was exploded with 125 ml. of oxygen. On adding caustic potash, there was a reduction of 80 ml. The remaining gas measuring 10 ml. was completely absorbed by alkaline pyrogallol. Find the composition of the mixture.

Total volume of the mixture = 45 ml.

Let the volume of methane = x ml.

and Volume of ethylene = y ml.

\therefore Volume of acetylene = $45-(x+y)$ ml.

Total volume of oxygen taken = 125 ml.

Volume of carbon dioxide = 80 ml.

(absorbed by KOH)

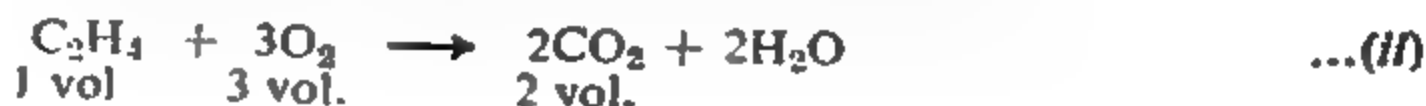
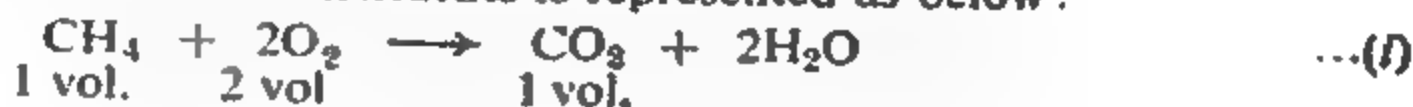
Volume of oxygen left unused = 10 ml.

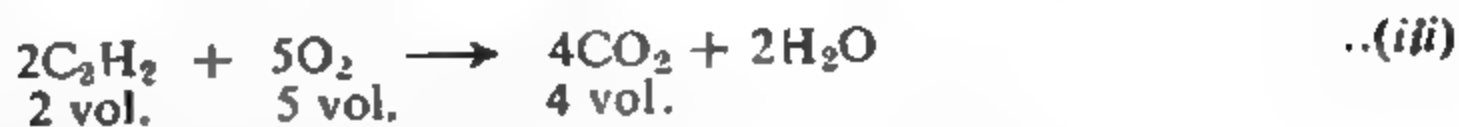
(absorbed by pyrogallol)

Volume of oxygen used for combustion = $125-10$

$$= 115 \text{ ml.}$$

The combustion of the three constituents is represented as below :





\therefore Volume of oxygen required for the combustion of x ml. of methane = $2x$ ml. (cf. equation i)

Volume of oxygen required for the combustion of y ml. of ethylene = $3y$ ml. (cf. equation ii)

Volume of oxygen required for the combustion of $[45 - (x + y)]$ ml. of acetylene = $5/2(45 - x - y)$ ml. (cf. equation iii)

$$\therefore \text{Total volume of oxygen required} = 2x + 3y + 5/2(45 - x - y) \quad \dots(\text{A})$$

$$\therefore 2x + 3y + 5/2(45 - x - y) = 115$$

Volume of CO_2 produced by the combustion of x ml. of methane = x ml. (cf. equation i)

Volume of CO_2 produced by the combustion of y ml. of ethylene = $2y$ ml. (cf. equation ii)

Volume of CO_2 produced by the combustion of $(45 - x - y)$ ml. of acetylene = $2(45 - x - y)$ ml. (cf. equation iii)

$$\therefore \text{Total volume of } \text{CO}_2 \text{ produced} = x + 2y + 2(45 - x - y) \quad \dots(\text{B})$$

$$\therefore x + 2y + 2(45 - x - y) = 80$$

From equations (A) and (B),

$$x = 10$$

$$\text{and } y = 15$$

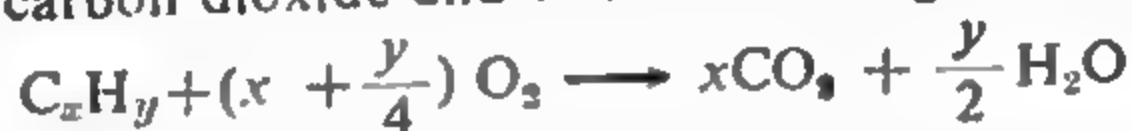
$$\therefore \text{Volume of methane} = 10 \text{ ml.}$$

$$\text{Volume of ethylene} = 15 \text{ ml.}$$

$$\text{Volume of acetylene} = 20 \text{ ml.}$$

MOLECULAR FORMULAE OF GASEOUS HYDROCARBONS

As already mentioned, all hydrocarbons burn in the presence of oxygen giving carbon dioxide and water according to the equation



Knowing the volume of carbon dioxide and of water produced by the combustion of a known volume of hydrocarbon, it is possible to calculate the molecular formula of the hydrocarbon *directly* without the prior knowledge of its percentage composition.

Suppose 10 ml. of a hydrocarbon on combustion produces 20 ml. of carbon dioxide and 30 ml. of water. From this data the molecular formula of the hydrocarbon can be determined as illustrated below :

10 ml. of the hydrocarbon produces 20 ml. of CO_2 and 30 ml. of H_2O

Or 1 volume of the hydrocarbon produces 2 volumes of CO_2 and 3 volumes of H_2O .

By Avogadro's law,

1 molecule of the hydrocarbon gives 2 molecules of CO_2 and 3 molecules of H_2O .

\therefore 1 molecule of the hydrocarbon contains 2 atoms of carbon and 6 atoms of hydrogen.

Thus, the molecular formula of the hydrocarbon is C_2H_6 .

Actual procedure. In order to determine the volume of carbon dioxide and that of water produced from a given volume of hydrocarbon, the following procedure is adopted :

(a) A known volume of the hydrocarbon is mixed with a measured excess of oxygen and ignited by an electric spark. The carbon and hydrogen of the hydrocarbon are converted into carbon dioxide and water vapour respectively. Since the experiment is carried out at the room temperature, the water vapour get condensed to liquid water. To ensure complete condensation of water vapour, the eudiometer tube is cooled after explosion. The volume occupied by liquid water is negligible since about 1700 ml. of water vapour on condensation produce only 1 ml. of liquid water.

The volume of the gaseous mixture after explosion and cooling is noted. Obviously, this volume gives the volume of carbon dioxide plus the volume of unused oxygen.

(b) In order to determine the volume of carbon dioxide formed, a little caustic soda or caustic potash is introduced into the eudiometer tube. The carbon dioxide is completely absorbed and thereby the mercury level rises upwards.

The decrease in volume on introducing caustic soda or caustic potash, evidently, gives the volume of carbon dioxide produced.

(c) The gas left in the tube after introducing caustic soda is the unused oxygen. Its volume is noted. From this, the volume of oxygen actually used for combustion is calculated.

(d) The next step is to calculate the volume of water vapour formed. This is done from the volume of the oxygen used for combustion, as shown below :

Let the total volume oxygen used = a ml.

Volume of CO_2 formed = b ml.

Since one volume of CO_2 is obtained from one volume of oxygen,



\therefore Volume of oxygen used for the production of carbon dioxide = the volume of CO_2 produced = b ml.

\therefore Volume of oxygen used for the production of water = $(a - b)$ ml. Since one volume of oxygen produces two volumes of water,



\therefore Volume of water vapour formed = $2(a - b)$

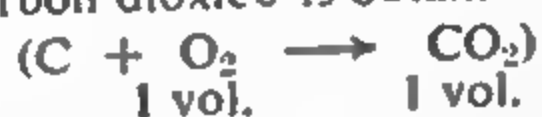
Knowing the volume of the hydrocarbon taken and the volume of carbon dioxide and water vapour produced on combustion, the molecular formula of the hydrocarbon can be calculated as illustrated above.

Example 1. 20 ml. of a gaseous hydrocarbon mixed with 100 ml. of oxygen were exploded in a eudiometer tube over mercury. After explosion and cooling, the gaseous volume was 70 ml. On introducing caustic soda solution, the volume was reduced to 10 ml. Calculate the molecular formula of the hydrocarbon.

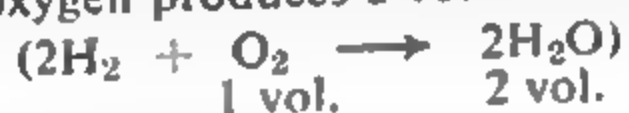
$$\begin{aligned} \text{Volume of the hydrocarbon taken} &= 20 \text{ ml.} \\ \text{Volume of oxygen taken} &= 100 \text{ ml.} \\ \text{Volume after explosion and cooling} &= 70 \text{ ml.} \\ \therefore \text{Volume of CO}_2 + \text{unused oxygen} &= 70 \text{ ml.} \\ \text{Volume of oxygen left unused} &= 10 \text{ ml.} \end{aligned}$$

$$\begin{aligned} \text{Reduction in volume on adding caustic potash} &\text{ viz., the volume of CO}_2 \\ &= 70 - 10 \\ &= 60 \text{ ml.} \\ \text{Volume of oxygen used} &= 100 - 10 \\ &= 90 \text{ ml.} \end{aligned}$$

Since 1 volume of carbon dioxide is obtained from 1 volume of oxygen,



$$\begin{aligned} \therefore \text{Volume of oxygen used for the production of 60 ml. of CO}_2 &= 60 \text{ ml.} \\ \therefore \text{Volume of oxygen used for the production of water} &= 90 - 60 = 30 \text{ ml.} \\ \text{Since 1 volume of oxygen produces 2 volumes of water,} \end{aligned}$$



$$\therefore \text{Volume of water produced by 30 ml. of oxygen used} = 60 \text{ ml.}$$

Thus, 20 ml. of the hydrocarbon on combustion produces 60 ml. of carbon dioxide and 60 ml. of water.

Or, 1 volume of the hydrocarbon produces 3 volumes of carbon dioxide and 3 volumes of water.

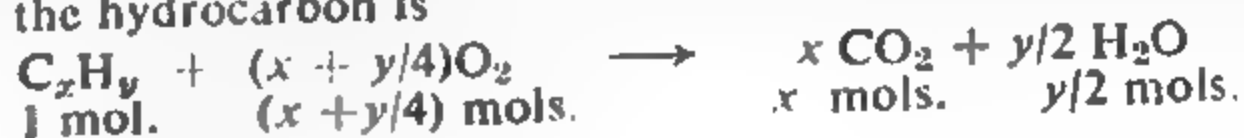
By Avogadro's law,

1 molecule of the hydrocarbon produces 3 molecules of CO₂ and 3 molecules of H₂O.

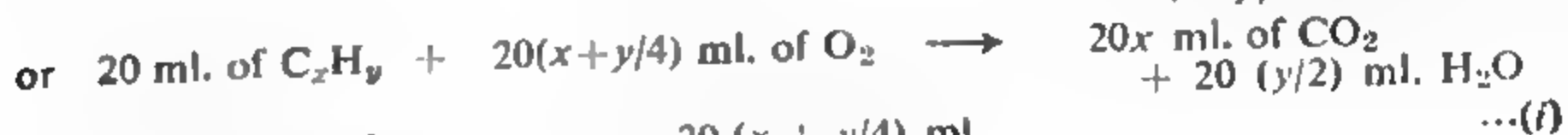
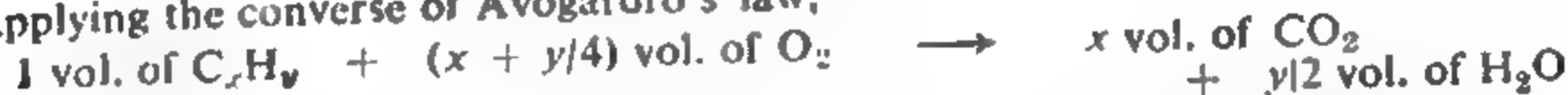
\therefore 1 molecule of the hydrocarbon contains 3 atoms of carbon and 6 atoms of hydrogen.

\therefore Molecular formula of the hydrocarbon is C₃H₆

Alternative Solution. Let C_xH_y be the formula of the hydrocarbon. The equation giving the combustion of the hydrocarbon is



Applying the converse of Avogadro's law,



$$\therefore \text{Oxygen used} = 20(x + y/4) \text{ ml.}$$

$$\therefore 20(x + y/4) = 90$$

$$\therefore \text{Carbon dioxide produced} = 20x \text{ ml}$$

$$\therefore 20x = 60$$

$$\therefore x = 3$$

$$\therefore y = 6$$

From (i) and (ii),

\therefore Molecular formula of the hydrocarbon is C₃H₆

Example 2. 25 ml. of a hydrocarbon were sparked with 85 ml. of oxygen. There was an immediate contraction in volume of 37.5 ml. On adding NaOH, there was a further contraction of 50 ml. Find the formula of the hydrocarbon.

Volume of the hydrocarbon taken = 25 ml.

Volume of oxygen taken = 85 ml.

∴ Total volume before explosion = 110 ml.

Contraction on explosion = 37.5 ml.

∴ Volume after explosion = $110 - 37.5$
 $= 72.5$ ml. (This is the volume of CO_2 + unused oxygen)

Contraction in volume on adding NaOH = 50 ml.

∴ Volume of carbon dioxide = 50 ml.

∴ Volume of oxygen left unused = $72.5 - 50$

$= 22.5$

Total volume of oxygen used = $85 - 22.5$

$= 62.5$ ml.

Proceeding further as in example 1, the volume of water formed comes out to be 25 ml. and the molecular formula of the hydrocarbon C_2H_2 .

Example 3. 10 ml. of a gaseous hydrocarbon required for complete combustion 238 ml of air (21 per cent of oxygen by volume) and the gaseous product occupied 218 ml. (all volumes being measured at N.T.P.) What is the molecular formula of the hydrocarbon? (Neglect the volume of water and use approximation to the nearest whole number of the volume of oxygen). (Pb. Inter 1956)

Volume of the hydrocarbon = 10 ml.

Volume of air taken = 238 ml.

Volume of oxygen in air = $\frac{21}{100} \times 238 = 49.98$
 $= 50$ ml.

∴ Volume of nitrogen in air = $238 - 50$
 $= 188$ ml.

Volume after explosion = 218 ml.

Since 238 ml. of air is required for complete combustion, no oxygen is left unused.

∴ The volume of 218 ml. consists of CO_2 + Nitrogen.

∴ Volume of CO_2 = $218 - 188$
 $= 30$ ml.

Proceeding further as in example 1, the volume of water comes out to be 40 ml. and the formula of hydrocarbon C_3H_8 .

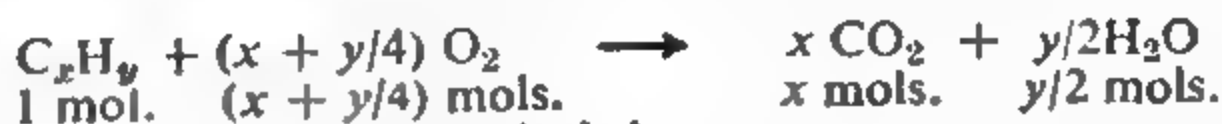
Example 4. 18 ml. of a gaseous hydrocarbon were exploded with excess of oxygen when there was a contraction of 54 ml. On adding KOH there was a further contraction of 54 ml. What is the molecular formula of the hydrocarbon?

Volume of hydrocarbon taken = 18 ml.

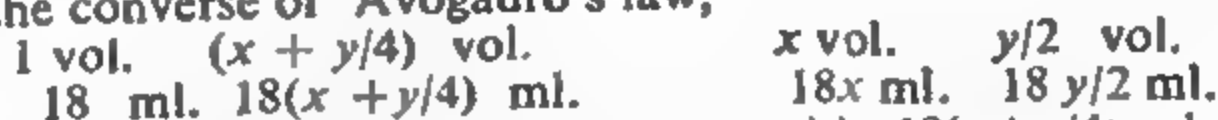
Contraction on explosion and cooling = 54 ml.

Volume of carbon dioxide = 54 ml.

Let C_xH_y be the formula of the hydrocarbon. The equation giving the combustion is :



Applying the converse of Avogadro's law,



That is, 18 ml. of the hydrocarbon react with $18(x + y/4)$ ml. of oxygen giving $18x$ ml. of CO_2 .

But the volume of CO_2 actually produced is 54 ml.

$$18x = 54$$

$$\therefore x = 3$$

Contraction in volume on combustion = Vol. before explosion - Vol. after explosion

$$= [18 + 18(x + y/4) + \text{excess oxygen}] - [18x + 18 y/2]$$

$$= 18 + 18(x + y/4) - 18x$$

$$\therefore 18x + 18(x + y/4) - 18x = 54$$

$$y = 8$$

$$\therefore \text{Formula of hydrocarbon} = C_3H_8$$

QUESTIONS

1. What are paraffins, olefins and acetylenes? Compare and contrast the properties of the three types of hydrocarbons.

2. Bring out clearly the significance of (i) a single bond (ii) a double bond and (iii) a triple bond.

3. How would you bring about the following conversions?

(i) Methane into Ethane and vice versa.

(ii) Ethane into Acetylene and vice versa.

(iii) Ethylene into Acetylene and vice versa.

4. How would you convert Methane into (i) Ethane (ii) Ethylene and (iii) Acetylene. Give three typical tests to distinguish between three compounds obtained. How would you effect their separation if present in a mixture?

5. Discuss the action of the following reagents on paraffins, olefins and acetylenes:

(i) Gaseous chlorine (ii) Bromine water (iii) Halogen acids (iv) Sulphuric acid (v) Ozone.

6. You are supplied with a mixture of gases containing carbon dioxide, methane, acetylene and ethylene. Explain with the help of equations, the method you would adopt for separating the constituents of the mixture. (Panjab Inter 1958)

7. How would you effect the separation of the constituents of a gaseous mixture containing ethane, acetylene and carbon dioxide? Explain fully the chemistry of the method you will employ and say how the separated constituents can be tested. (Panjab Inter 1949)

8. 'While the paraffin hydrocarbons react by substitution, the olefins react by addition.' Illustrate and explain the statement. Point out clearly the main difference in the reactions of the two types of hydrocarbons. (Panjab Inter 1946)

9. Starting from Ethane, show how you can obtain (a) Methane (b) Propane (c) Ethylene (d) Acetylene. Mention the important differences between the types of hydrocarbons formed.

10. 15 ml. of a gaseous hydrocarbon required for complete combustion 327 ml. of air (21 percent oxygen by volume) and the gaseous products occupied 327 ml. (all volumes being measured at N.T.P.). What is the formula of hydrocarbon? (Neglect the volume of water and use approximation to the nearest whole number of the volume of oxygen) (Ans. C_3H_8) (U.P. Inter 1954)

11. 10 ml. of gaseous hydrocarbon were mixed with 30 ml. of oxygen in a eudiometer tube and exploded. After cooling, the residual gas occupied 20 ml. On adding

KOH, there was further contraction to 10 ml. Find the formula of the hydrocarbon. (Ans. CH_4) (*Panjab Inter 1960*)

12. 52 ml. of a gaseous hydrocarbon was exploded with an excess of oxygen and the product cooled. A contraction of 7.8 ml. was observed. A further contraction of 10.4 ml. was noted on treatment with aqueous potash. Find out the molecular formula of the hydrocarbon. (Ans. CH_4) (*Panjab Inter 1957*)

13. 15 ml. of a mixture of hydrogen and acetylene required 19.5 ml. of oxygen for complete combustion. Calculate the composition of the mixture by volume. (Ans. Hydrogen = 9 ml. Acetylene = 6 ml) (*Panjab Inter 1956 Suppl.*)

14. 20 ml. of a gaseous hydrocarbon were exploded with 100 ml. of oxygen. On cooling to the room temperature, the volume of the gaseous mixture was found to be 70 ml. Introduction of caustic potash reduced the volume to 10 ml. the residual gas being only oxygen. Calculate the molecular formula of the hydrocarbon. What likely structural formula would you assign to it? (Ans. C_3H_6) (*Panjab Inter 1953*)

15. 15 c.c. of a gaseous hydrocarbon was mixed with excess of oxygen (say 90 c.c.) and exploded in a eudiometer tube. The explosion was followed by a contraction of 45 c.c. Introduction of caustic potash into the eudiometer tube brought about a further contraction of 45 c.c. What was the hydrocarbon? (Ans. C_3H_8) (*Panjab Inter 1952 Suppl.*)

16. Calculate the composition by volume of a mixture of carbon monoxide and methane 10.5 c.c. of which required 9.0 c.c. of oxygen for its complete combustion. (Ans. $\text{CO} = 8$ c.c. $\text{CH}_4 = 2.5$ c.c.) (*Panjab Inter 1955 Inorganic*)

17. 12 c.c. of a gaseous hydrocarbon are exploded with an excess of oxygen. A volume contraction of 24 c.c. is observed. Also when the residual gases were treated with potassium hydroxide solution a further volume contraction of 24 c.c. is observed. What is the formula of the hydrocarbon, given that the volumes of gases were measured at 0°C and 760 mm pressure throughout. (Ans. C_2H_4) (*Madras Inter 1948*)

CHAPTER XXIX

PETROLEUM AND ITS PRODUCTS

Petroleum is decidedly the most abundant source of the aliphatic as well as cyclic hydrocarbons. It occurs in large amounts as a dark viscous oily liquid in underground deposits in different parts of the earth.

Petroleum was known to Red Indians as a thin oily film on the surface of certain ponds in Pennsylvania (U.S.A.) and was used by them as a medicament. Colonel Darke is reported to have drilled the first oil well at a place in Pennsylvania in 1859. The demand for petroleum has been ever on the increase and since then about 3000 billion gallons of petroleum has been brought to the surface according to very conservative estimates. A new branch of knowledge known as Petroleum Technology has been developed.

In certain areas, mostly in the U.S.A., large quantities of gaseous hydrocarbons, generally the first six members of the alkane series, occur in association with or without petroleum. This gaseous mixture is known as natural gas. It is carried by a network of pipe lines from the field to the factory or wherever needed. It is an excellent fuel.

Some countries are very fortunate in possessing big oil fields and this has, to a very large extent, been responsible for their industrial development and prosperity. The U.S.A., in particular, is an example. It contains nearly 65 percent of the total world's occurrence of petroleum. Russia comes next with about 11 per cent. Venezuela, Iran, Rumania, Mexico and Columbia also contain oil fields in decreasing order. In all, there are about twenty-six countries which can be put on the petroleum map of the world. But most of them, excepting those mentioned above, contain insignificant amounts. India, for instance, accounts for only about 0.01 percent of the world's occurrence and depends for almost all her requirements upon foreign imports. But prospecting for oil is now being extensively pursued by the Oil and Natural Gas Commission of India and there is a reasonable hope that fresh oil fields will be explored and the dependence on foreign imports will be reduced, if not eliminated altogether.

Composition. Petroleum is a complex mixture of innumerable hydrocarbons—gaseous, liquids and solids. The hydrocarbons are largely of two types : (i) the paraffins, ranging from the lowest member methane to the highest member $C_{10}H_{22}$ and (ii) the cycloparaffins, that is, the saturated hydrocarbons with ring structures. A certain amount of aromatic and olefinic hydrocarbons is also present. *The exact composition of petroleum varies with the location of oil field.*

The usual composition of natural gas is as given below :

Methane 83%, Ethane 9%, Propane 4%, Butane 2%, Higher hydrocarbons. 2%.

Origin of petroleum. The origin of petroleum is still uncertain. A number of theories have been proposed but none of them is satisfactory. According to the modern view, petroleum is formed by the decomposition of animal and vegetable remains under pressure and high temperature, in the interior of the earth. The decomposition is initiated either by some bacteria followed by several stages, physical and chemical changes, or catalysed by certain inorganic substances present in the interior of the earth. Many chemists believe that both the processes are operating at different stages.

Mining of petroleum. Petroleum deposits occur at a depth of several thousand feet (varying from place to place), usually associated with sand

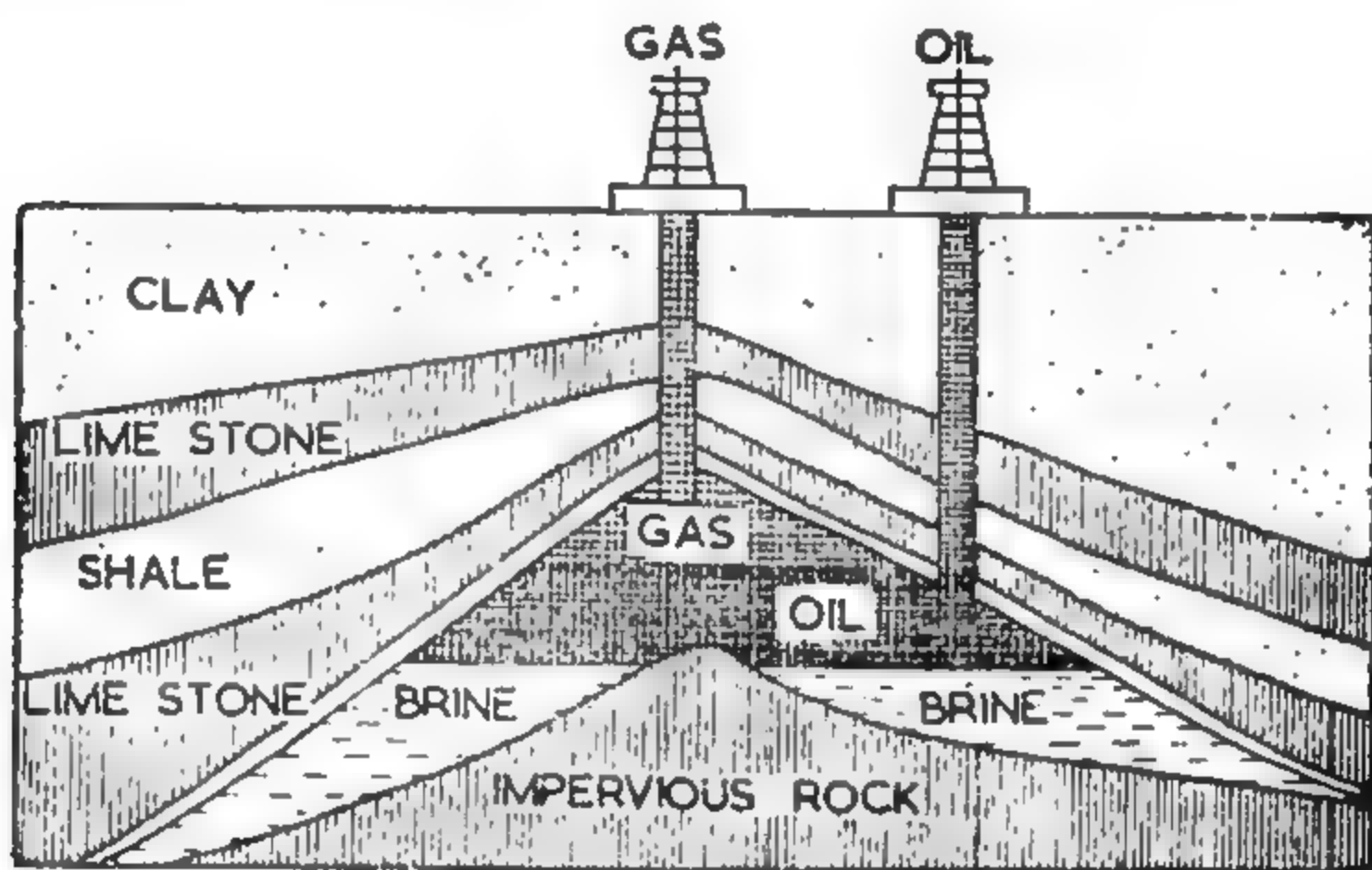


Fig. 1. Occurrence and Extraction of Petroleum

and under different layers and folds of rocks of different types, as shown in Fig. 1. It is only rarely that petroleum gushes out, of itself, due to its own pressure. Usually a well has to be drilled through the various layers till the oil-bearing strata are reached. The petroleum is then raised to the surface by means of suitable pumps and transported by means of pipes to refineries located far off from the fields.

Refining of petroleum. The crude petroleum contains a large variety of organic compounds of great utility. Till comparatively recently the main demand on petroleum was for its kerosene oil which was used for lighting purposes. The lighter fractions (low boiling) and heavier fractions (high boiling) were considered to be of no use and were thrown away. But now with the invention of combustion engine used in motor cars, air planes, and in other contrivances the demand for lighter fractions has increased beyond all proportions. The demand for kerosene oil, on the contrary, has decreased with the development of cheap means of producing electricity. The tendency, therefore, is to convert

kerosene oil and even higher fractions into lighter fractions by a process known as cracking. The demand for higher fractions for lubrication, water proofing, etc., has also gone up a great deal in recent years. In fact, every drop of petroleum is considered precious. It is rightly called liquid gold.

The entire series of processes by which raw petroleum is converted into number of useful products is known as refining. The main operations involved are :

1. Fractional distillation or straight distillation.
2. Cracking, viz., conversion of higher into lower fractions.

Fractional Distillation. By means of fractional distillation, crude petroleum is separated into a number of fractions each boiling or passing over at a definite temperature range. Each fraction is a mixture of

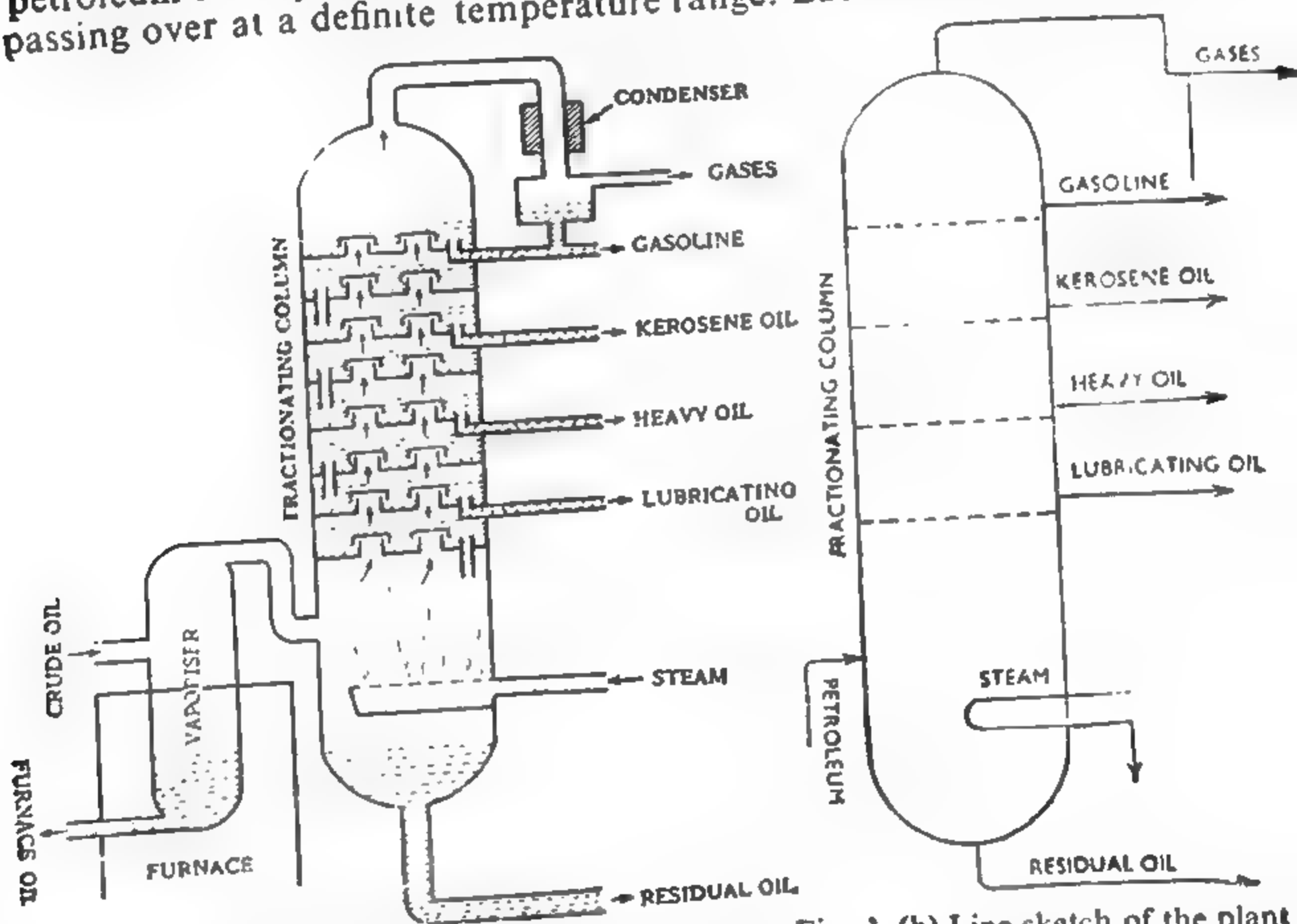


Fig. 2. (a) Fractionation of Petroleum

Fig. 2. (b) Line sketch of the plant

different hydrocarbons and has certain characteristics which render them useful for definite purposes. The names of the various fractions, their boiling ranges and chief applications are given in Table 1.

The type of the fractionating column used for the fractional distillation is shown in Fig. 2 (a) and a line sketch of the plant is shown in Fig. 2 (b). It consists of a tall column made of steel having perforated shelves so as to bring about intimate contact between the vapours distilling over and the liquid condensing and running back down the column. As already explained in chapter XVIII the effect of using such a column is to concentrate the lower boiling constituents in the rising vapour and the higher boiling constituents in

the liquid which condenses and flows down the column. The lowest boiling fraction condenses at the top and the highest boiling fraction at the bottom, as shown in the figure. Thus, by using a fractionating column of a suitable length, with outlets at suitable intervals, it is possible to separate crude petroleum into different fractions as shown in Table 1.

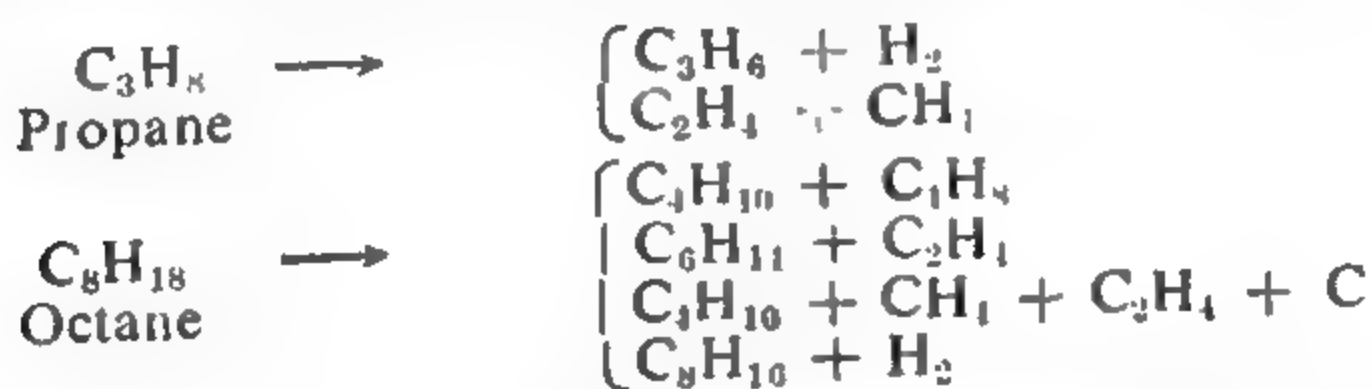
TABLE 1
Fractions obtained from Petroleum

Serial No.	Main fraction with boiling range	Refractionated products with boiling range	Approximate Composition	Uses
1	Petroleum gases —164° to 30		$C_1 - C_4$	Fuels, making carbon black.
2	Gasoline 30 —200°	(i) Petroleum ether (30—90°)	$C_5 - C_7$	Solvent, dry cleaning, refrigeration
		(ii) Gasoline or Petrol (40—200)	$C_7 - C_9$	Solvent, motor fuel.
3	Kerosene oil 200°—300	(i) Lamp oil (200—250°) (ii) Paraffin for heating (iii) Paraffin for tractors	$C_{10} - C_{16}$	Lighting, fuel for stoves, manufacture of oil gas.
4	Fuel Oil 300 —400	(i) Gas oil (ii) Diesel Oil (iii) Furnace oil	$C_{16} - C_{20}$	Fuel for diesel engines and tractors, cracking stocks.
5	Lubricating oil 350 —400	(i) Medicinal oil (ii) Motor oil (iii) Grease	C_{20} upwards	Paint oil, transformer oil, lubrication, sizing paper.
6	Wax 400 upwards	(i) Petroleum (ii) Paraffin Wax (iii) Road asphalt (iv) Petroleum cake	C_{24} upwards	Ointment, candles, paraffin wax for matches, water proofing, solid fuel, protective paint.

2 Cracking of Oils. By the process of fractional distillation, hardly about 20 per cent of the petroleum comes out in the petrol or gasoline fraction. The demand for petrol as a motor fuel is much higher. Therefore, a very large amount of gasoline is prepared by converting heavier fractions (such as kerosene oil, fuel oil, etc.) into gasoline. *This process of breaking down of the less volatile higher hydrocarbon molecules in different types of more volatile lower hydrocarbons is called cracking.*

The cracking is carried out usually in the temperature range lying between 400 and 700°. The pressure varies from 3 to 50 atmospheres. In the presence of catalyst, cracking can be done at lower temperatures (400—500°) and lower pressures.

The chemical reactions involved in cracking are highly complex and somewhat obscure. The process may involve (i) the rupture of carbon to carbon bonds resulting in the transformation of a larger into simpler molecules (ii) the rupture of carbon-hydrogen bonds giving hydrogen accompanied by partial carbonization. For instance,



Synthetic Petroleum

The limited sources for the supply of petroleum and the ever increasing rate at which it is being consumed, has stimulated attempts to synthesise fuels from alternative sources.

Coal occurs more abundantly than petroleum. It is not pure carbon. It contains appreciable amounts of hydrogen as well. But its hydrogen content is less and carbon content is more than that present in liquid fuel gasoline. So the problem is to introduce more hydrogen and take away a part of carbon.

Two processes are employed for the production of synthetic petroleum.

(i) *Bergius Process.*

(ii) *Fischer-Tropsch Process.*

(1) **Bergius Process.** In this process the coal is well pulverised mixed with the catalyst (usually an organic compound of tin) and made into a paste with 50 per cent heavy oil in the 'mixer' (cf. Fig. 3). It is then heated to 400—500° in hydrogen under a pressure of 200—250 atmospheres in the 'converter'. Hydrogenation of the coal takes place resulting in the formation of higher hydrocarbons. These on cracking and simultaneous hydrogenation produce mixtures of alkanes. These compounds on condensation yield synthetic petroleum or crude oil. This

is subjected to fractional distillation in the 'fractionating column' to get the various fractions in the usual manner.

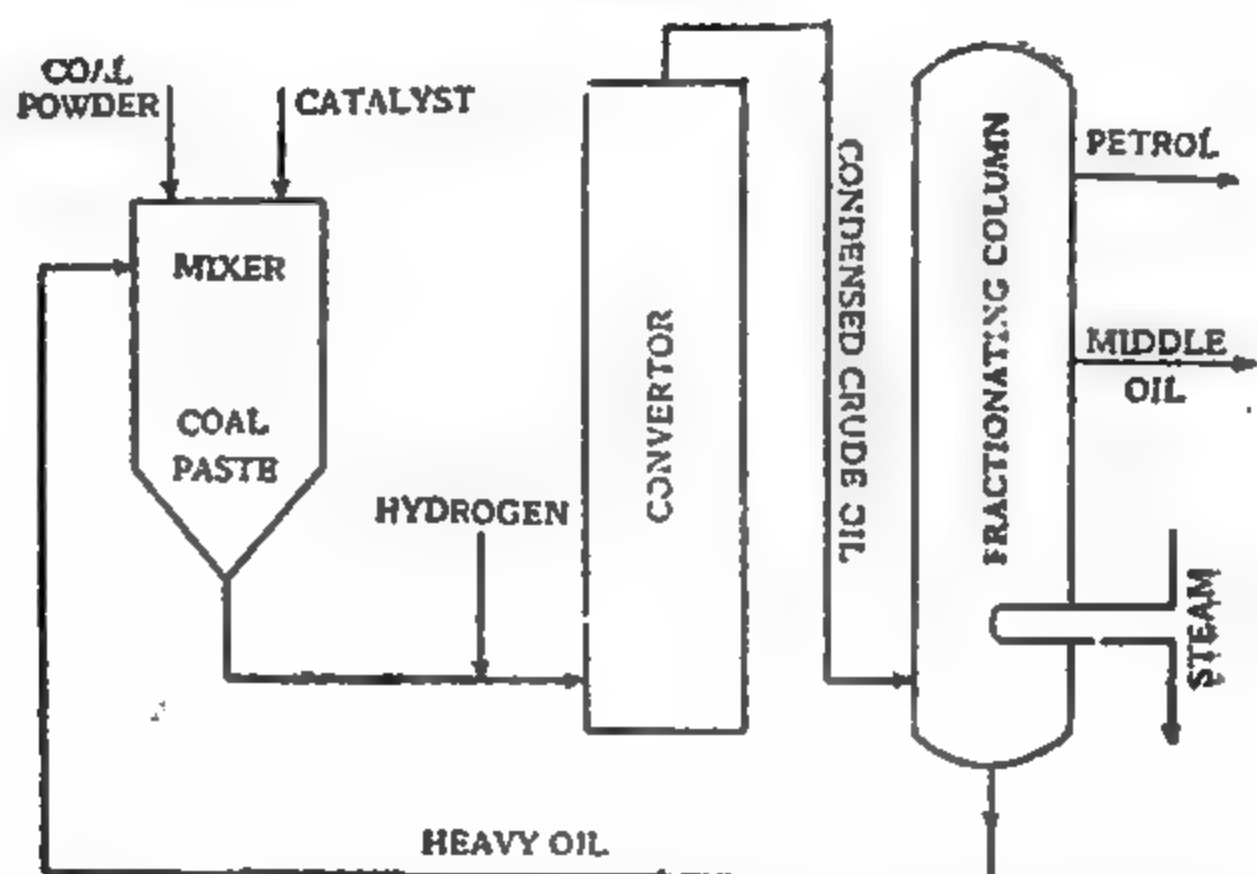


Fig. 3. Synthetic Petroleum from Coal by Bergius Process

(2) **Fischer-Tropsch process.** In this process the water gas obtained by the action of steam on coke



is mixed with half of its volume of hydrogen so that the gaseous mixture consists of carbon monoxide and hydrogen in the ratio of 1 : 2. This mixture is then heated to 250° under a pressure of 1–10 atmospheres and passed over a 'cobalt catalyst' when petroleum is formed. The reaction may be represented by the equation



The synthetic petroleum obtained above is then distilled in the usual manner to get petrol, kerosene oil, lubricating oil and paraffin wax.

Flash Point. Not long ago when there was very little demand for low boiling fractions (such as gasoline) of petroleum, the temptation in commercial circle was to include these fractions also in the kerosene oil. This was highly risky because the lower boiling fractions give off vapours which catch fire whenever a flame of any sort is brought near. Thus, there was a danger of fire even when a match stick was lighted in the surroundings. Therefore, several governments enacted laws according to which kerosene oil used for lighting and burning purposes should not give off vapour which could catch fire below a certain minimum temperature, known as the flash point.

The minimum temperature at which the vapours above an oil give a flash of light, when a flame is brought near, is known as the flash point.

The flash point fixed for a particular oil varies from country to country, depending upon the climate. Obviously, it is high for a hot country like India while it is low for a cold country like Britain.

Determination of Flash Point. A simplified form of Abel's apparatus for determining flash point is shown in Fig. 4. The oil is placed in a beaker which is fitted with a wide bored cork. Two platinum electrodes pass through the cork and are held just above the oil at a distance of 5—10 mm. from each other as shown. A thermometer also passes through the cork and dips into the oil. There is an arrangement for stirring as well. A small watch glass covers the wide hole in the cork.

The water bath is gradually heated. The platinum electrodes are connected to an induction coil and sparking is allowed to take place between them. As the flash point approaches, the vapour will catch fire and due to expansion, the watch glass will be lifted with a gentle explosion. The temperature in the oil is then noted. This gives the flash point.

Oil Gas. The oil gas used in the laboratory is prepared by the cracking of kerosene oil. The plant is shown in Fig. 5. The kerosene oil is introduced gradually into the red hot iron retort where it is heated strongly and gets cracked, that is gets converted into lower gaseous hydrocarbons. A good deal of tarry

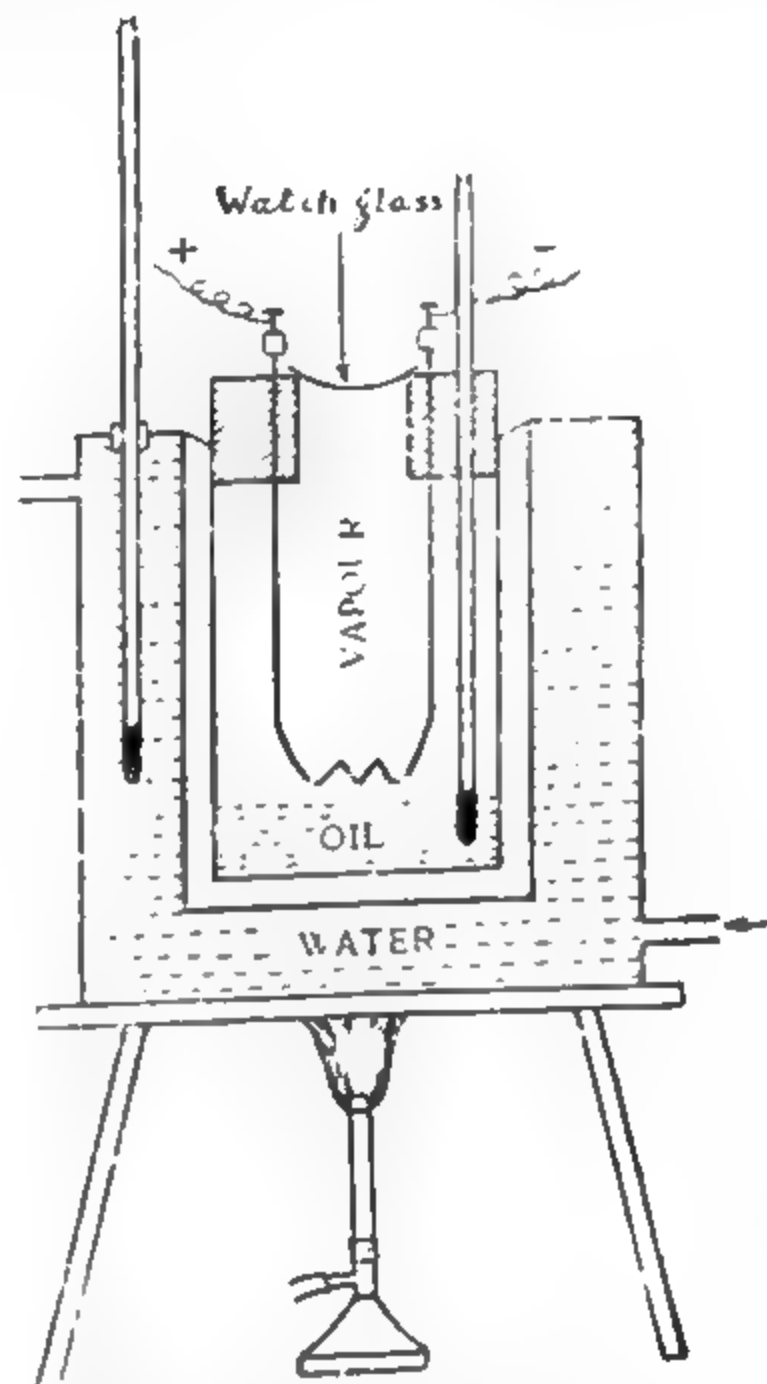


Fig. 4. Abel's Flash Point apparatus.

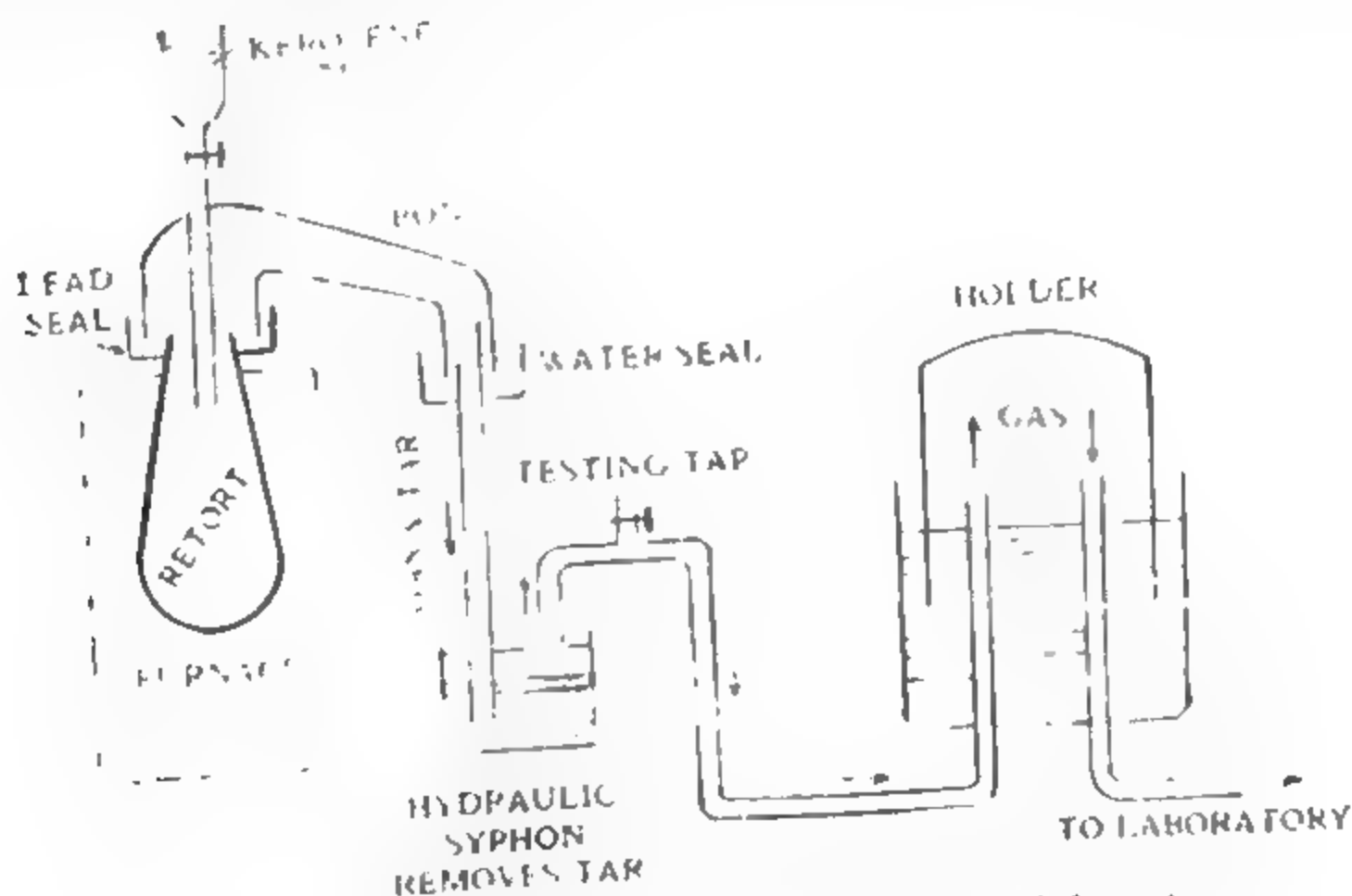


Fig. 5. Preparation of Oil Gas for use in the laboratory.

matter of volatile nature is also produced at the same time and gets mixed up. The gas, therefore, passes through a hydraulic siphon where tar condenses as dark oily liquid. The gas is finally collected in big metallic gas holders over water and conveyed to laboratory through pipes, whenever required.

Petrol Gas. When only a small supply of gas is needed and that too occasionally, it is more convenient to instal a petrol gas plant. In this plant, the petrol is converted into lower gaseous hydrocarbons by the usual process of cracking. The petrol is converted into vapour and passed through electrically heated coils when petrol gas results.

QUESTIONS

1. What is petroleum ? How does it occur ? Describe the various fractions obtained from it and mention the industrial uses to which they are put.

2. Describe the methods for getting gasoline or petrol from crude petroleum. How is gasoline purified ?

3. "Petroleum is liquid gold". Justify statement.

4. Explain the term cracking. Describe how gasoline and oil gas can be obtained by cracking.

5. What is a Flash point ? What is its importance ? Describe a simple method for the determination of flash point.

6. What gas is used in the laboratory for heating purposes ? How is it prepared ? What is petrol gas ?

7. How is Petrol obtained from petroleum ? Enumerate the by-products and their uses ?
(*Panjab Inter 1961 Suppl.*)

8. Name the four main fractions obtained during refining of petroleum. To what commercial uses are they put ?
(*Panjab Inter 1959*)

9. Explain the following terms as used in petroleum Industry :

(i) Flash Point

(ii) Gasoline

(iii) Cracking of oils

(iv) Benzine

Give the utility of each.

(*Panjab Inter 1953 Suppl.*)

10. Explain what you understand by the terms :

(i) Natural gas (ii) Cracking of Oils (iii) Flash point.

Give an elementary idea of getting synthetic petrol. (*Panjab Inter 1952 Suppl.*)

11. "Cracking is said to be breaking up larger molecules into simpler ones." Comment upon the statement with suitable examples.

Enumerate applications of cracking.

12. Give briefly fractionation of petroleum. Name the fractions and mention industrial uses to which they are put.
(*Panjab ; T.D.C Part I 1964 S*)

CHAPTER XXX

HALOGEN DERIVATIVES OF PARAFFINS

Halogen derivatives of paraffins are obtained by replacement of one or more hydrogen atoms of the paraffins by the halogen atoms. These are named as *mono*, *di*, *tri*, or *tetra* halogen derivatives depending upon the number of halogen atoms in the molecule. Since these halogen atoms can be easily replaced by other atoms or groups, the halogen derivatives serve as important synthetic reagents in organic chemistry. These compounds do not occur in nature. They are always prepared in laboratory.

MONO HALOGEN DERIVATIVES OR ALKYL HALIDES.

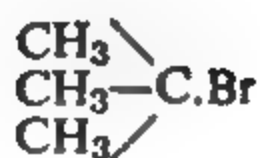
The general formula of alkyl halides is $R-X$ where R is an alkyl radical such as methyl, ethyl, propyl, etc., and X is a halogen atom such as Cl , Br or I .

Nomenclature. There are two ways in which these compounds can be named :

(i) **Common nomenclature.** This is based on the name of the alkyl radical and on the halogen atom present in the compound. For example, CH_3Cl is called methyl chloride and CH_3CH_2Br is called ethyl bromide. Further, if the halogen atom is attached to a primary or a secondary or a tertiary carbon atom, the corresponding compound will be termed as *normal* or *iso* or *tertiary* alkyl halide.

(ii) **I. U. C. nomenclature.** According to I. U. C. system, these compounds are named as substitution products of the corresponding alkanes. The name of the halogen is mentioned before that of the alkane and the position is indicated by the lowest possible number. The names of a few compounds according to the above two systems are given below

Formula	Common name	I. U. C. name
CH_3Cl	Methyl chloride	Chloromethane
CH_3CH_2Br	Ethyl bromide	Bromoethane
$CH_3CH_2CH_2I$	n-Propyl iodide	1-Iodopropane
$\begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \end{array} > CHCl$	Isopropyl chloride	2-Chloropropane

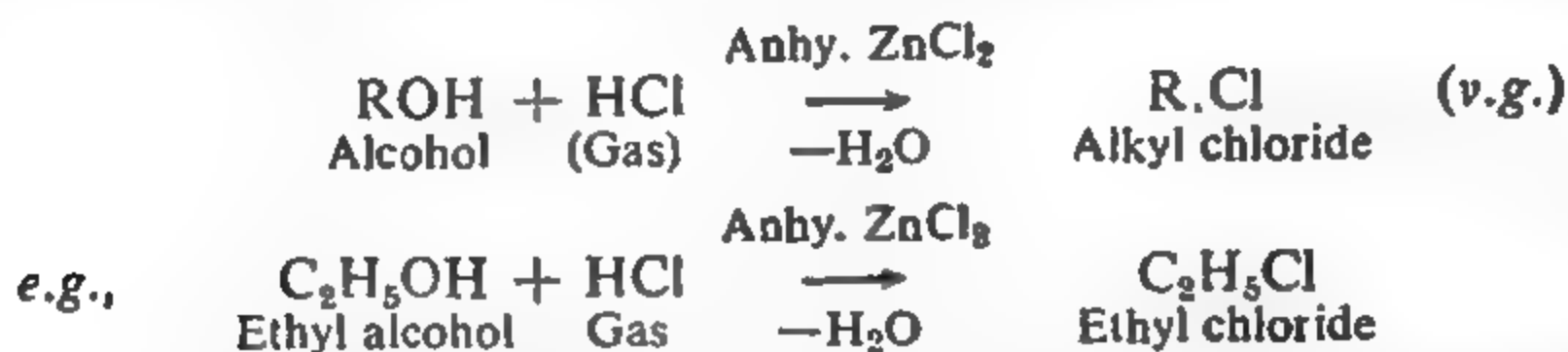


Tert. Butyl bromide

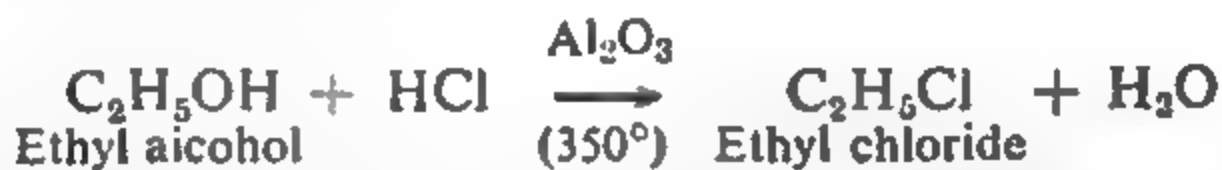
2-Bromo 2-methyl
propane

General Methods of Preparation. 1. **From alcohols.** The most convenient method of preparing alkyl halides is by replacing the hydroxyl group of an alcohol by a halogen atom.

(i) Alkyl chlorides, but not bromides and iodides, are obtained by saturating the alcohol with hydrogen chloride gas in the presence of anhydrous ZnCl_2 which acts as a dehydrating agent (*Grove's method*).



(ii) All halides (chlorides, bromides and iodides) can be prepared by passing a mixture of alcohol vapour and hydrogen halide over heated alumina. For example,



(iii) In the laboratory, alkyl bromides (or iodides) are prepared by heating the alcohol with a mixture of potassium bromide (or iodide) with concentrated sulphuric acid, *e.g.*,



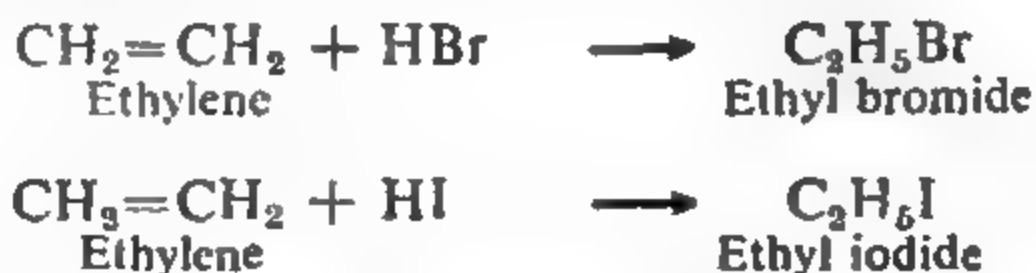
For better yields, sulphuric acid is replaced by phosphoric acid.

(iv) Alkyl halides can also be prepared by the action of phosphorus halides on alcohols.



This is a very convenient method for the preparation of alkyl halides. Yields are *excellent* for primary alcohols, and *good* for secondary and tertiary alcohols.

2. **From olefins.** Alkyl halides can also be obtained by the addition of hydrogen halides to an olefin. For example,



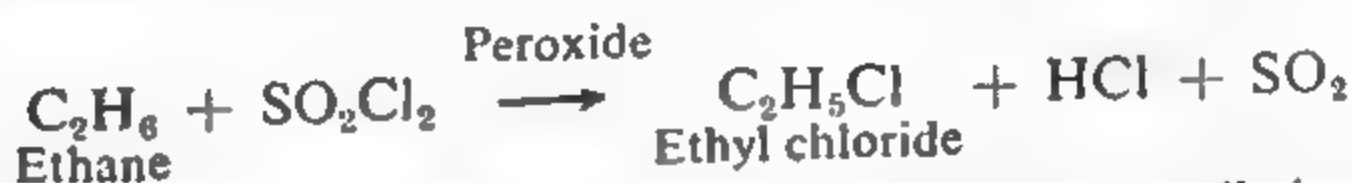
In case of higher members, addition of hydrogen halide is governed by *Markownikoff's rule*.

3. **From alkanes.** (i) *Direct halogenation.* Alkanes can be converted into alkyl halides by treatment with halogens in the presence of light and heat or a catalyst. For example,



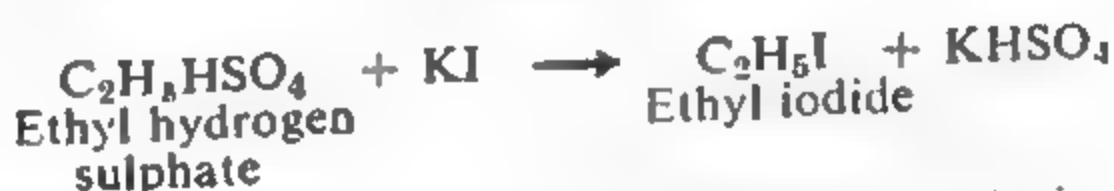
However, this method yields a mixture of halides such as CH_2Cl_2 , CHCl_3 , etc., and is of little utility.

(ii) *By treatment with sulphuryl chloride.* Recently chlorination of alkanes has been carried out by means of sulphuryl chloride (SO_2Cl_2) in the presence of light and a trace of an organic peroxide (catalyst), e.g.,



4. **From other Sources.** Alkyl halides can also be obtained from alkyl sulphates and silver salts of fatty acids as shown below :

(i) *From alkyl sulphates.* By the action of metallic halides in aqueous solution, e.g.,



(ii) *From silver salt of fatty acids* By the action of chlorine or bromine (not iodine).

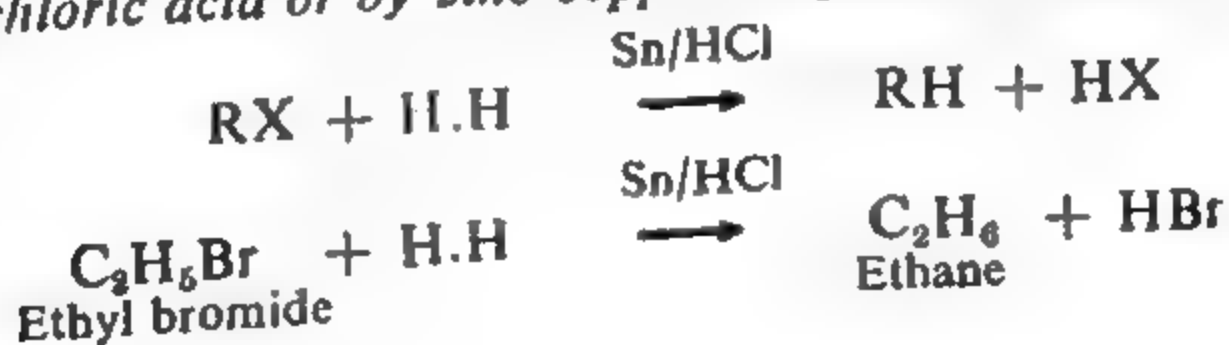


Physical Properties. The lower members, methyl chloride, methyl bromide and ethyl chloride are gases under ordinary conditions. Methyl iodide and the majority of the higher members are colourless, pleasant smelling liquids. The members with still higher molecular weights are colourless solids.

Alkyl halides are practically insoluble in water but dissolve readily in organic solvents.

Chemical Properties. Alkyl halides are extremely reactive organic compounds because the halogen atom is in a loose combination with the carbon atom and can be easily replaced by almost all other groups or atoms. Thus, a large variety of compounds can be prepared from the alkyl halides as illustrated below :

1. **Preparation of paraffins.** (i) Alkyl halides, when reduced by tin and hydrochloric acid or by zinc-copper couple and alcohol, give paraffins.



(ii) When treated with *sodium metal in the presence of dry ether*, two molecules of the alkyl halide join to form higher paraffins (Wurtz reaction).



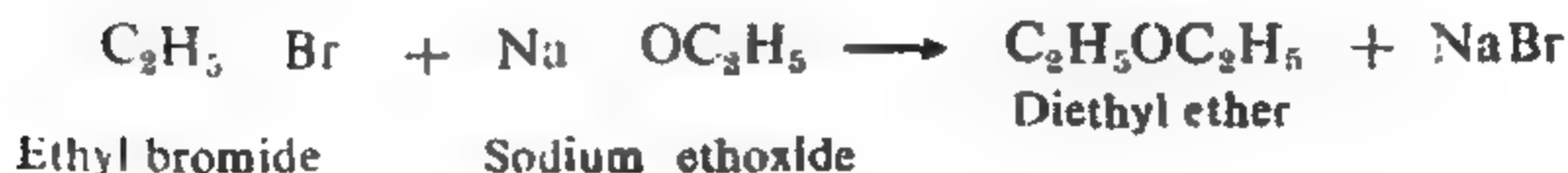
2. Preparation of olefins. When an alkyl halide is heated with *alcoholic potash*, a molecule of the hydrogen halide is eliminated resulting in the formation of olefins. For example, ethylene can be obtained from ethyl halides :



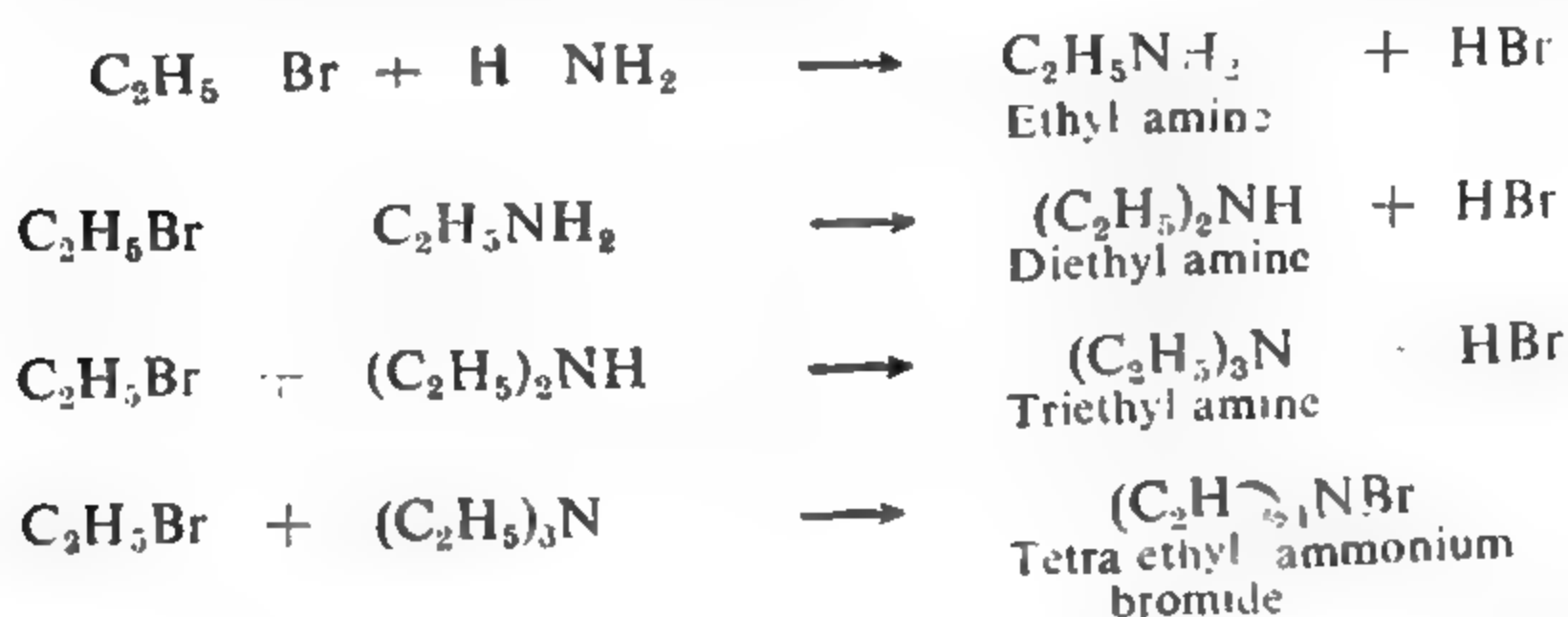
3. Preparation of alcohols. When treated with *aqueous potash* or *moist silver oxide*, viz., AgOH, the alkyl halides yield alcohols.



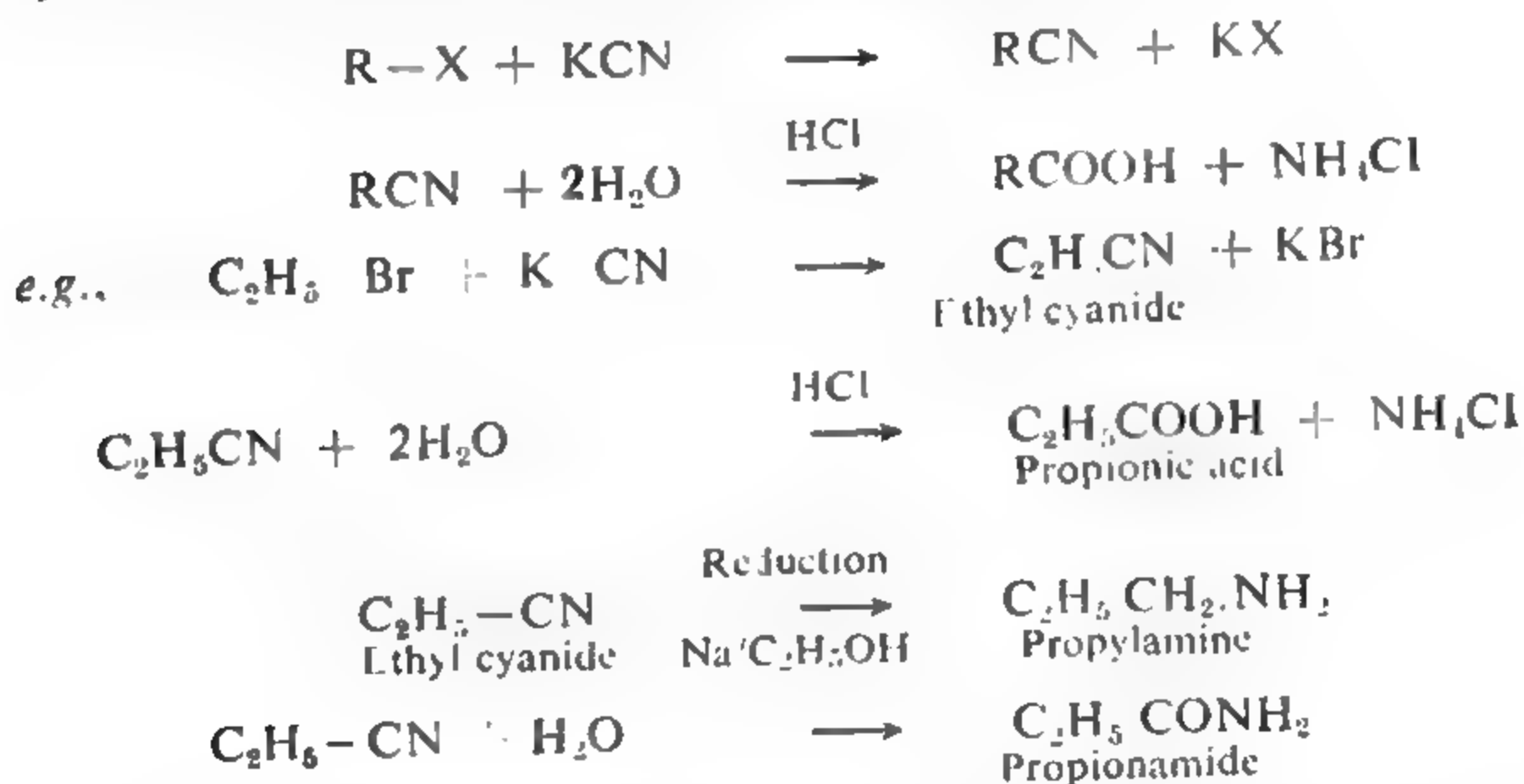
4. Preparation of ethers. When heated with *dry silver oxide* or with *sodium alcoholates*, alkyl halides give ethers.



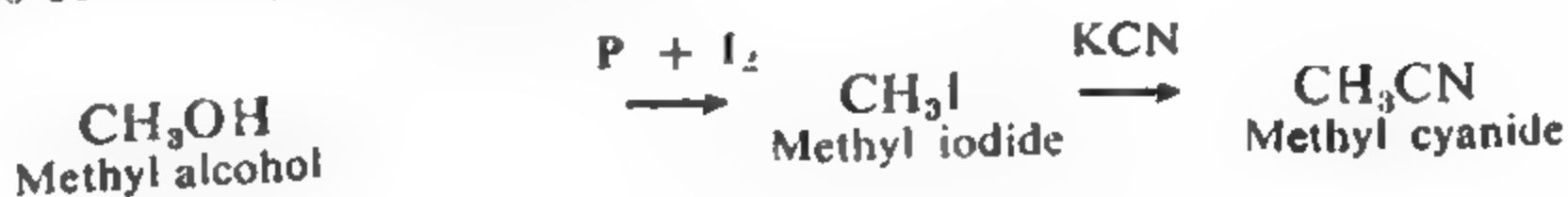
5. Preparation of amines. When heated with an *alcoholic solution of ammonia in a sealed tube*, alkyl halides give a mixture of primary, secondary, tertiary amines and the quaternary ammonium salt. For example,

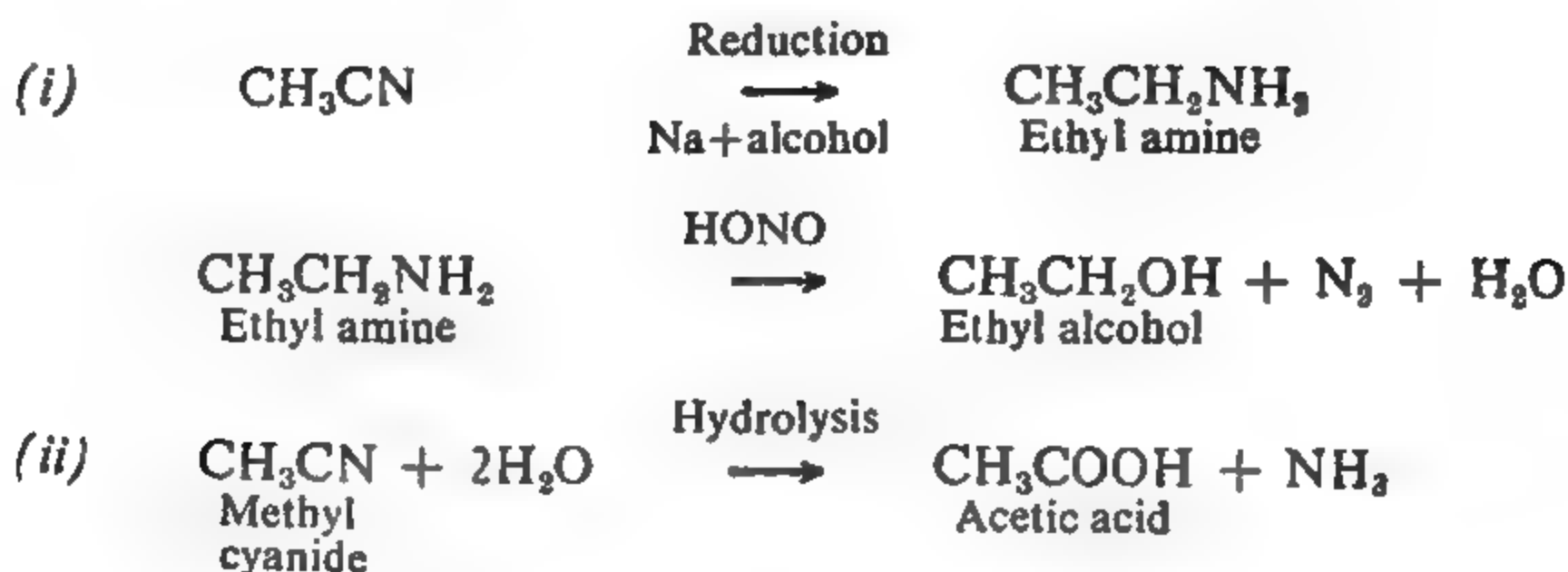


6. Preparation of nitriles (cyanides), carboxylic acids, primary amines and amides. On treatment with an *alcoholic solution of potassium cyanide*, alkyl halides give the corresponding cyanides, which on subsequent hydrolysis in the presence of mineral acids in excess, yield carboxylic acids and on reduction with sodium and alcohol, a primary amine. Partial hydrolysis of alkyl cyanides yield the corresponding amides.



Since the conversion of an alkyl halide into alkyl cyanide involves the addition of one carbon into the molecule, it places at our disposal a means of **ascending a homologous series, i.e., the conversion of a lower member into the higher one.** For example, methyl alcohol (a derivative of methane) can be converted into ethyl alcohol or acetic acid (both derivatives of ethane) as follows :

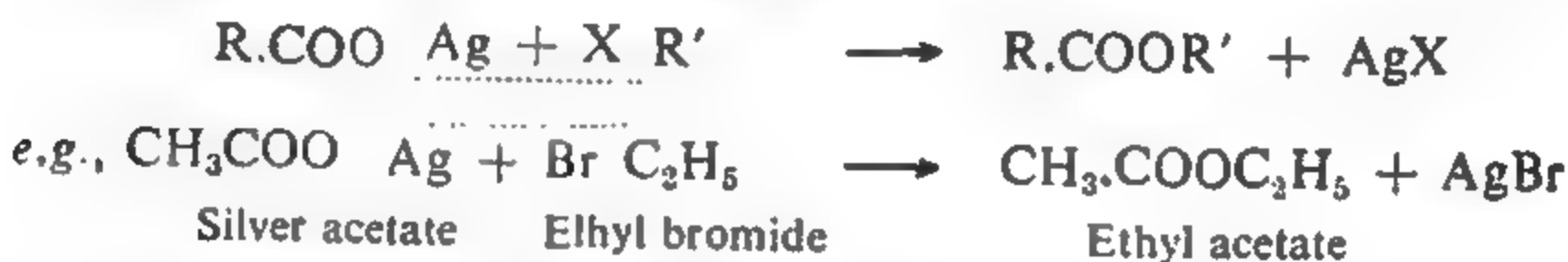




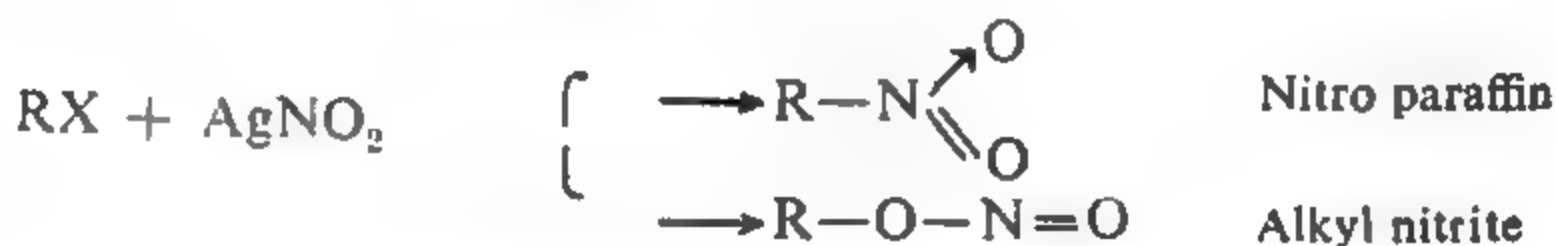
7. **Preparation of isocyanides.** On treatment with *silver cyanide* alkyl halides give alkyl isocyanides.



8. **Preparation of esters.** Alkyl halides react with *silver salts of fatty acids* yielding the corresponding esters.



9. **Preparation of nitroparaffins and alkyl nitrites.** When distilled with *silver nitrite*, the alkyl halides yield a mixture of nitro paraffins and alkyl nitrites, the main product being the **nitro-compound**.

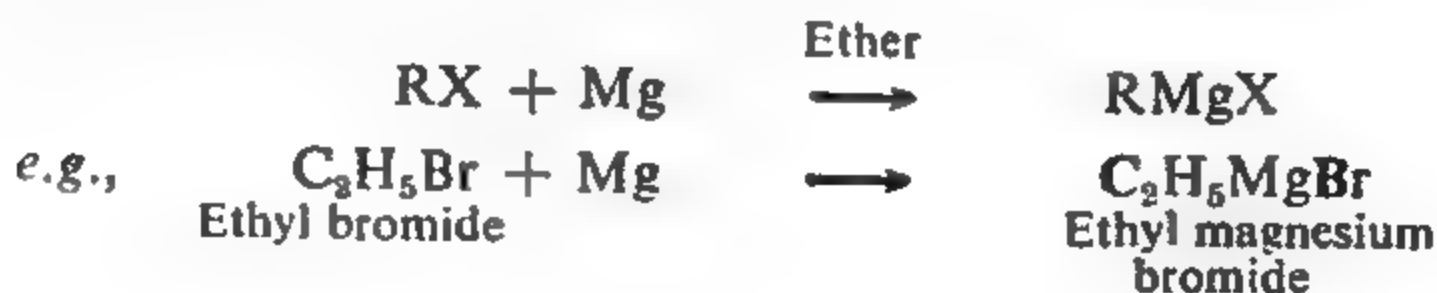


With *potassium nitrite* the main product is an **alkyl nitrite**.

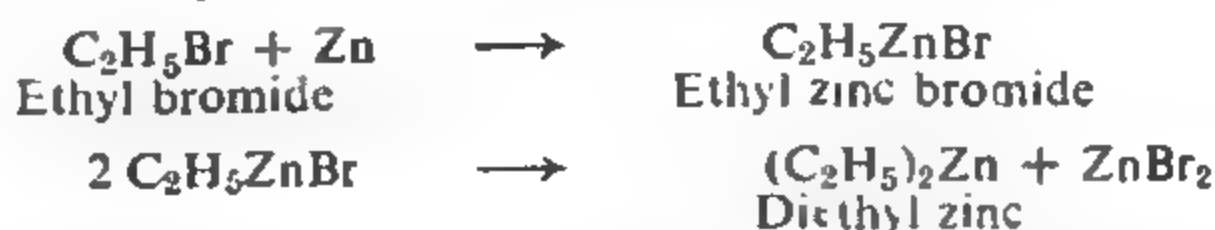


10. **Preparation of organo-metallic compounds.** Alkyl halides on treatment with *active metals* like magnesium and zinc give rise to **organo-metallic compounds**. For example,

(i) On treatment with *pure dry* magnesium in the presence of *dry* ether, an alkyl magnesium halide, known as **Grignard reagent**, is produced.



(ii) On distilling with zinc filings in an atmosphere of carbon dioxide, zinc alkyls are formed. For example,



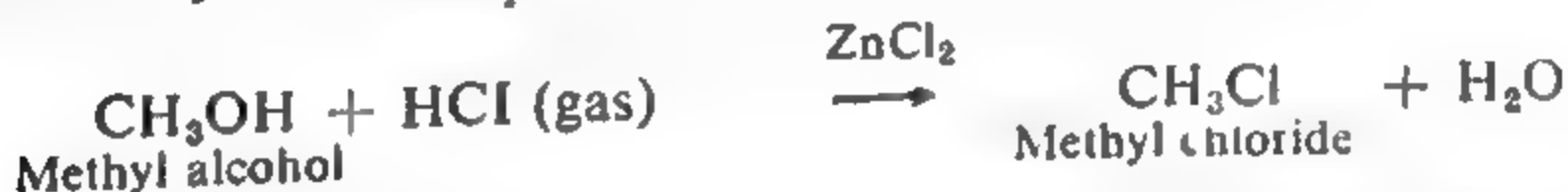
These organo-metallic compounds are extremely *important synthetic reagents* and are used for preparing a large variety of organic compounds.

INDIVIDUAL MEMBERS

Methyl Chloride or Chloromethane, CH_3Cl

Preparation. Methyl chloride is prepared on an industrial scale by the following methods :

(1) *By the action of hydrogen chloride gas on methyl alcohol in the presence of anhydrous zinc chloride (Grove's Process)*



(2) *By the direct chlorination of methane.* Methane, when chlorinated in the presence of cupric chloride, gives methyl chloride.



To avoid the formation of CH_2Cl_2 , CHCl_3 and CCl_4 , chlorine is diluted with nitrogen in a suitable proportion.

(3) *By heating trimethyl amine hydrochloride with hydrochloric acid at 360° under pressure.*



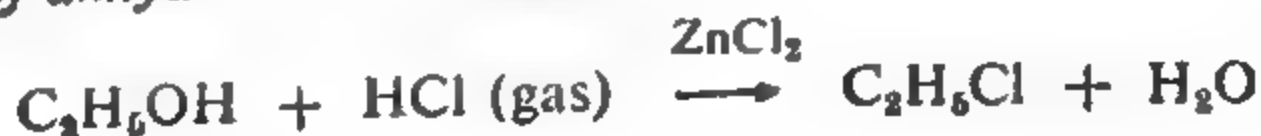
Properties and Uses. Methyl chloride is a colourless gas with a sweet smell. It is fairly soluble in water and readily so in ethyl alcohol. Liquid methyl chloride boils at -24° . It gives all the reactions of a typical alkyl halide (cf. chemical properties of alkyl halides).

It is used (i) in the manufacture of amine dyes (ii) as a refrigerant (iii) as a local anaesthetic (iv) as a methylating agent (v) as a solvent for the extraction of perfumes and (vi) as a fire extinguisher.

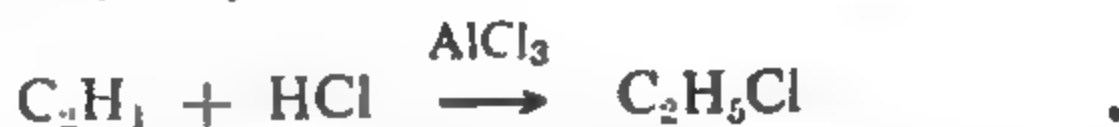
Ethyl Chloride or Chloroethane, $\text{C}_2\text{H}_5\text{Cl}$

Ethyl chloride is prepared on a commercial scale by the following two processes :

(1) *By the action of hydrogen chloride gas on ethyl alcohol in the presence of anhydrous zinc chloride.*



(2) By the addition of hydrogen chloride to ethylene in the presence of aluminium chloride (catalyst).



Properties and Uses. Ethyl chloride is a sweet smelling gas under ordinary conditions. Liquid ethyl chloride boils at 12.5° . It gives all the reactions typical of alkyl halides (see general properties).

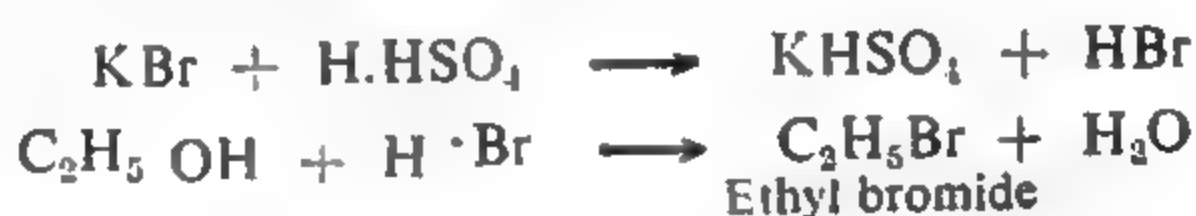
It is used (i) as a local anaesthetic (ii) in the preparation of tetraethyl lead (iii) as refrigerant and (iv) as an ethylating agent.

Ethyl Bromide or Bromoethane, $\text{C}_2\text{H}_5\text{Br}$

Preparation. Ethyl bromide is prepared on a large scale by passing a mixture of ethylene and hydrogen bromide vapour through a suspension of aluminium bromide in ethyl bromide (catalyst) at a low temperature.



(ii) **Laboratory preparation.** In the laboratory, ethyl bromide is conveniently prepared by distilling a mixture of potassium bromide, ethyl alcohol and concentrated sulphuric acid.



The apparatus used for the purpose is shown in Fig. 1.

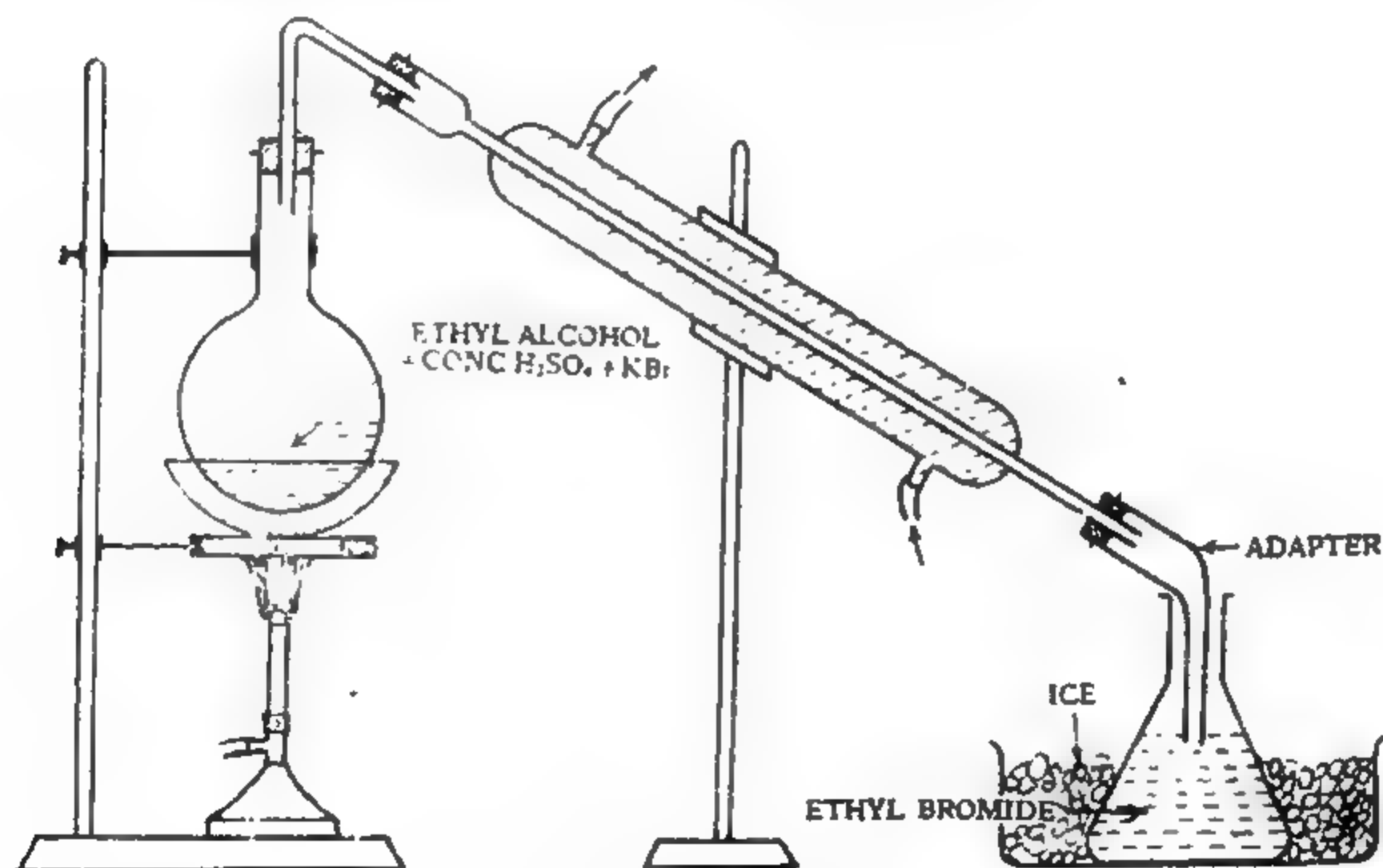


Fig. 1. Preparation of ethyl bromide.

60 gm. of ethyl alcohol is mixed with 50 gm. of water in a one-litre round-bottom flask and 200 gm. of concentrated sulphuric acid is added gradually by constant shaking and cooling. 100 gm. of powdered potassium bromide is then added, shaking and cooling being continued. The flask is connected with the condenser and rapid distillation is carried out by heating the flask on a sand bath. Ethyl bromide distils over and collects as a heavy oily liquid in a receiver which is kept in ice bath. Distillation is continued till no more oily drops fall into the receiver.

Ethyl bromide is separated from water by means of a separating funnel. It is washed first with its own volume of water, then with a dilute solution of sodium carbonate and finally with water. This is done to free it from bromine, hydrobromic acid and alcohol. Ethyl bromide so obtained is transferred to a dry conical flask and some anhydrous granular calcium chloride is added to it. When the liquid becomes clear (usually after 3–4 hours), it is decanted into a distillation flask and redistilled. Pure ethyl bromide distils over at about 38° – 39° . It is sealed in a glass tube.

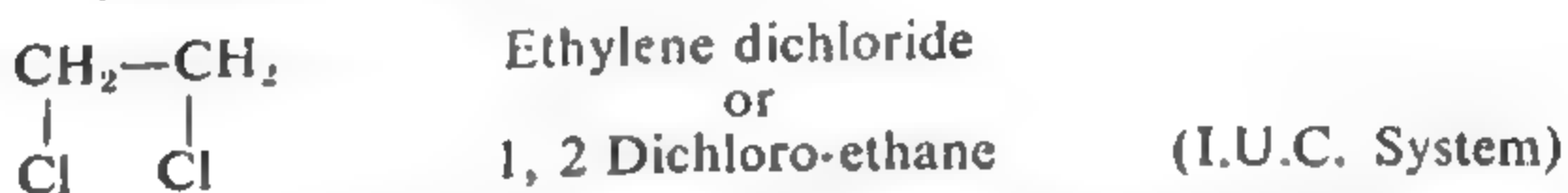
Properties and Uses. Ethyl bromide is a colourless liquid with a pleasant smell. It boils at 38.4° . In chemical properties it resembles ethyl chloride (see general properties of alkyl halides).

It is used as an ethylating agent as well as a reagent for organic syntheses.

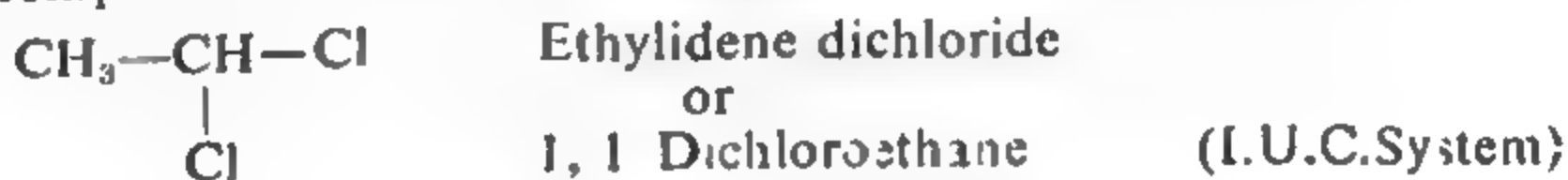
DIHALOGEN DERIVATIVES

Dihalogen derivatives are obtained by the replacement of two hydrogen atoms of the paraffins by halogen atoms. For example, CH_2Cl_2 , dichloromethane or methylene chloride, is obtained from methane.

When two halogen atoms enter the molecule of an alkane other than methane, they may attach to the same or to different carbon atoms. When the halogens are linked to *different carbon atoms*, the compounds are called **alkylene dihalides**. For example,



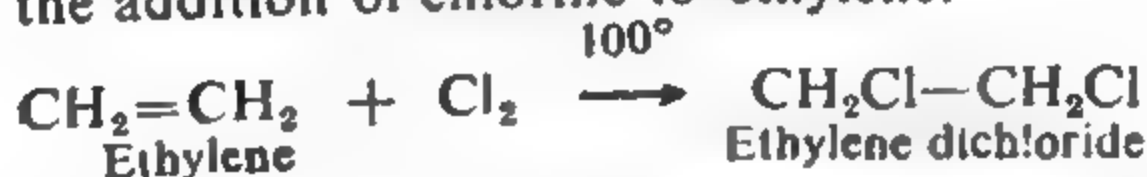
When the two halogens are attached to the *same carbon atom*, the resulting compounds are named **alkylidene dihalides**. For example,



Ethylene Dichloride (1, 2 Dichloroethane,) $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$.

It is obtained :

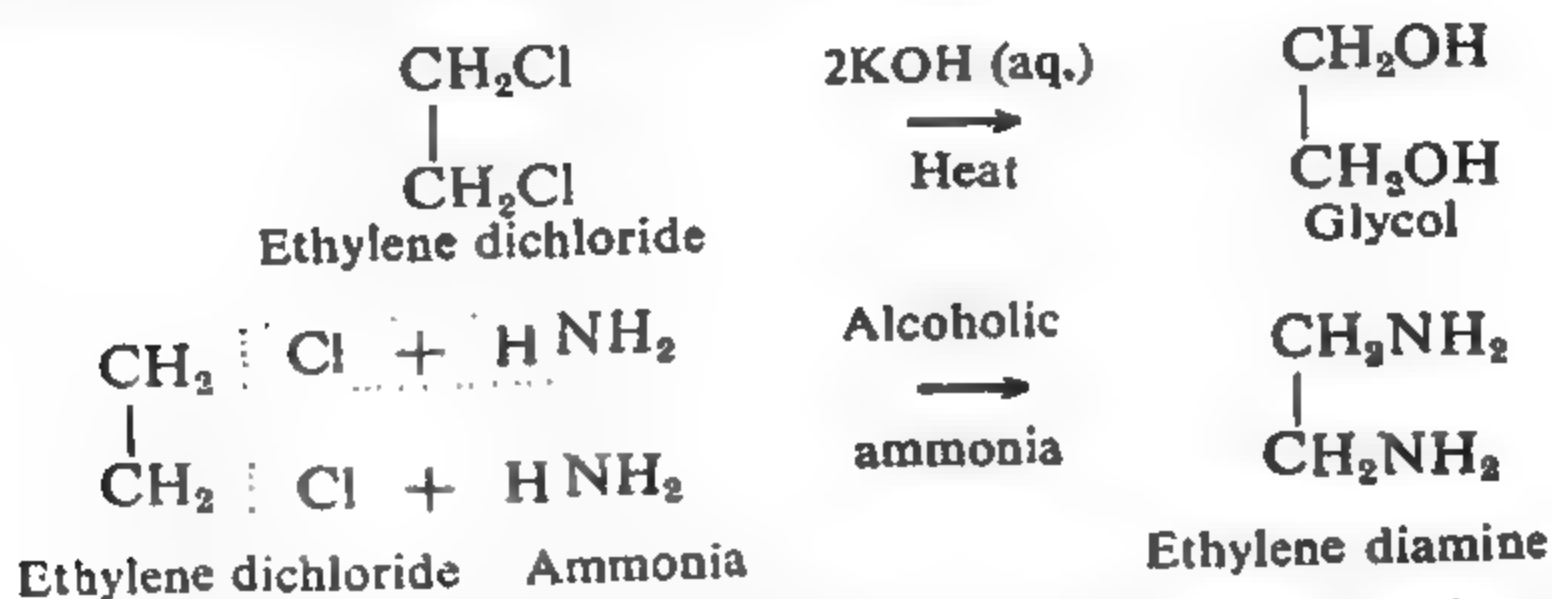
(i) By the addition of chlorine to ethylene.



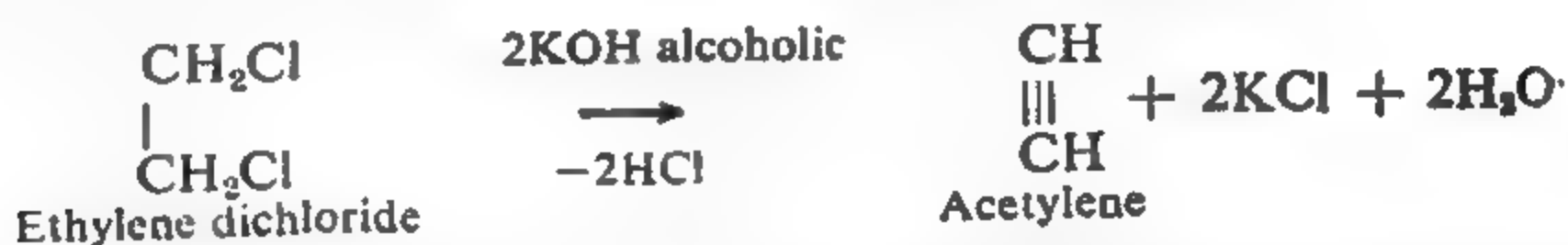
(ii) By the action of hydrochloric acid on glycol.



Ethylene dichloride is a colourless, pleasant smelling liquid boiling at 84° . It gives all the reactions of alkyl halides. Thus, both the chlorines can be replaced by H , $-\text{OH}$, $-\text{NH}_2$, or $-\text{CN}$, on interaction with hydrogen, aqueous potash, alcoholic ammonia or potassium cyanide respectively, under suitable conditions. For instance,



On treatment with alcoholic potash, it yields acetylene.



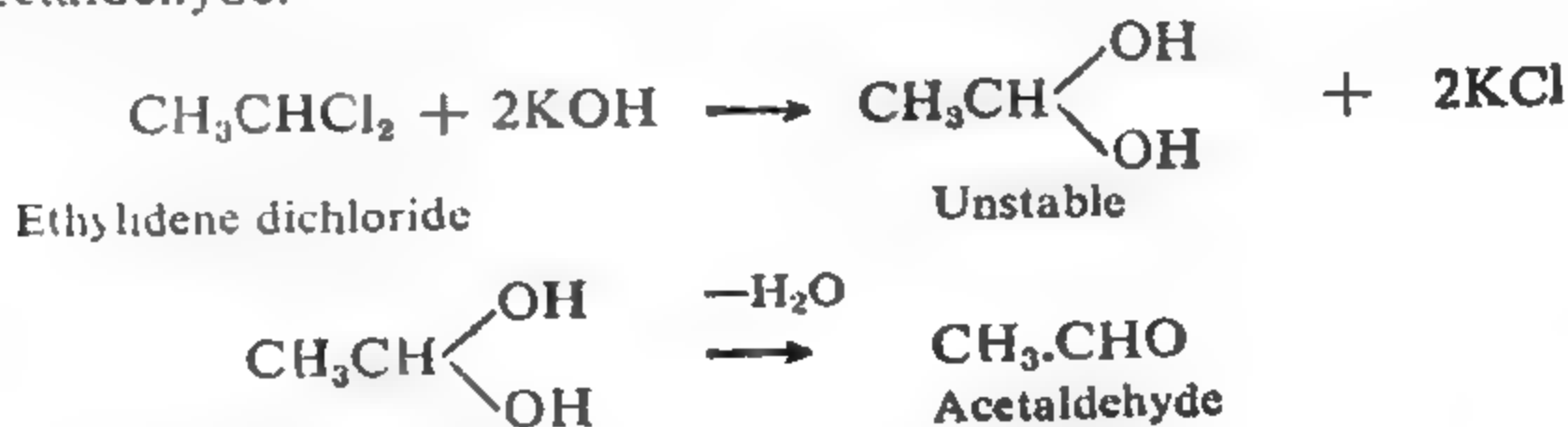
Ethylene dichloride is a stable, non-flammable liquid and is used as a solvent for fatty materials and also in the preparation of insecticides. Ethylene dichloride combines with sodium tetra-sulphide, Na_2S_4 , to form *thiokol* used as a substitute for rubber.

Ethylidene Dichloride (1, 1 Dichloroethane), CH_3CHCl_2

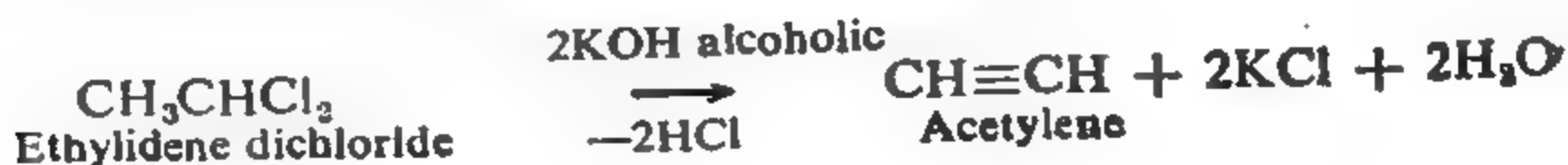
It may be prepared by the action of phosphorus pentachloride on acetaldehyde or by the addition of hydrochloric acid to acetylene.



Ethylidene dichloride is a colourless liquid boiling at 57.3° . It is less reactive than ethylene dichloride. When boiled with aqueous potash it gives acetaldehyde.



With alcoholic potash, it also gives acetylene.



The distinctive features of ethylene dichloride and ethylidene dichloride are summed up in Table 1.

TABLE 1.
Distinctive features of $C_2H_4Cl_2$ and CH_3CHCl_2

Property	Ethylene dichloride $C_2H_4Cl_2$	Ethylidene dichloride CH_3CHCl_2
1. Boiling Point	84°	57.3°
2. Hydrolysis with aqueous potash.	Gives glycol	Gives acetaldehyde
3. Reaction with active metals like zinc or magnesium.	Gives ethylene	Gives butylene

TRIHALOGEN DERIVATIVES

These are derived from alkanes by replacing three hydrogen atoms by halogens. The most important trihalogen derivatives are those of methane. These are:

$CHCl_3$ Trichloromethane or chloroform
 $CHBr_3$ Tribromomethane or bromoform
 CHI_3 Tri-iodomethane or iodoform.

Out of these, chloroform and iodoform are more useful and are described below.

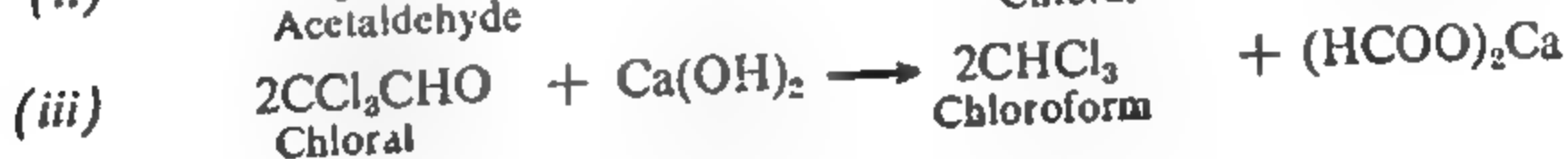
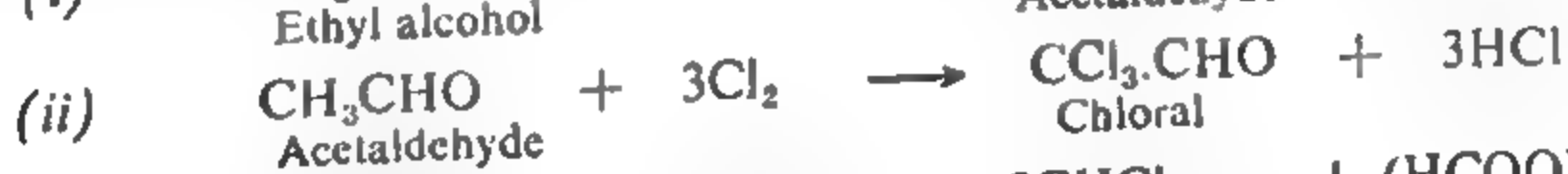
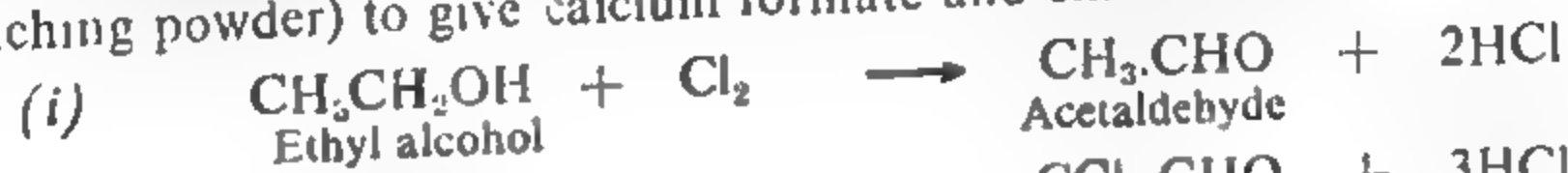
Chloroform, Trichloromethane, $CHCl_3$

Preparation. 1. Chloroform is prepared in the laboratory as well as on a commercial scale by heating ethyl alcohol (or acetone) with bleaching powder.

The reaction is extremely complicated and the mechanism is obscure.

The equations which are usually given to represent the reaction between alcohol and bleaching powder involve:

- (i) The oxidation of ethyl alcohol to acetaldehyde.
- (ii) Chlorination of acetaldehyde to tri-chloroacetaldehyde (chloral).
- (iii) Hydrolysis of chloral by free calcium hydroxide (obtained from bleaching powder) to give calcium formate and chloroform.



In the case of acetone, the first product is trichloroacetone which is then hydrolysed to chloroform and calcium acetate :

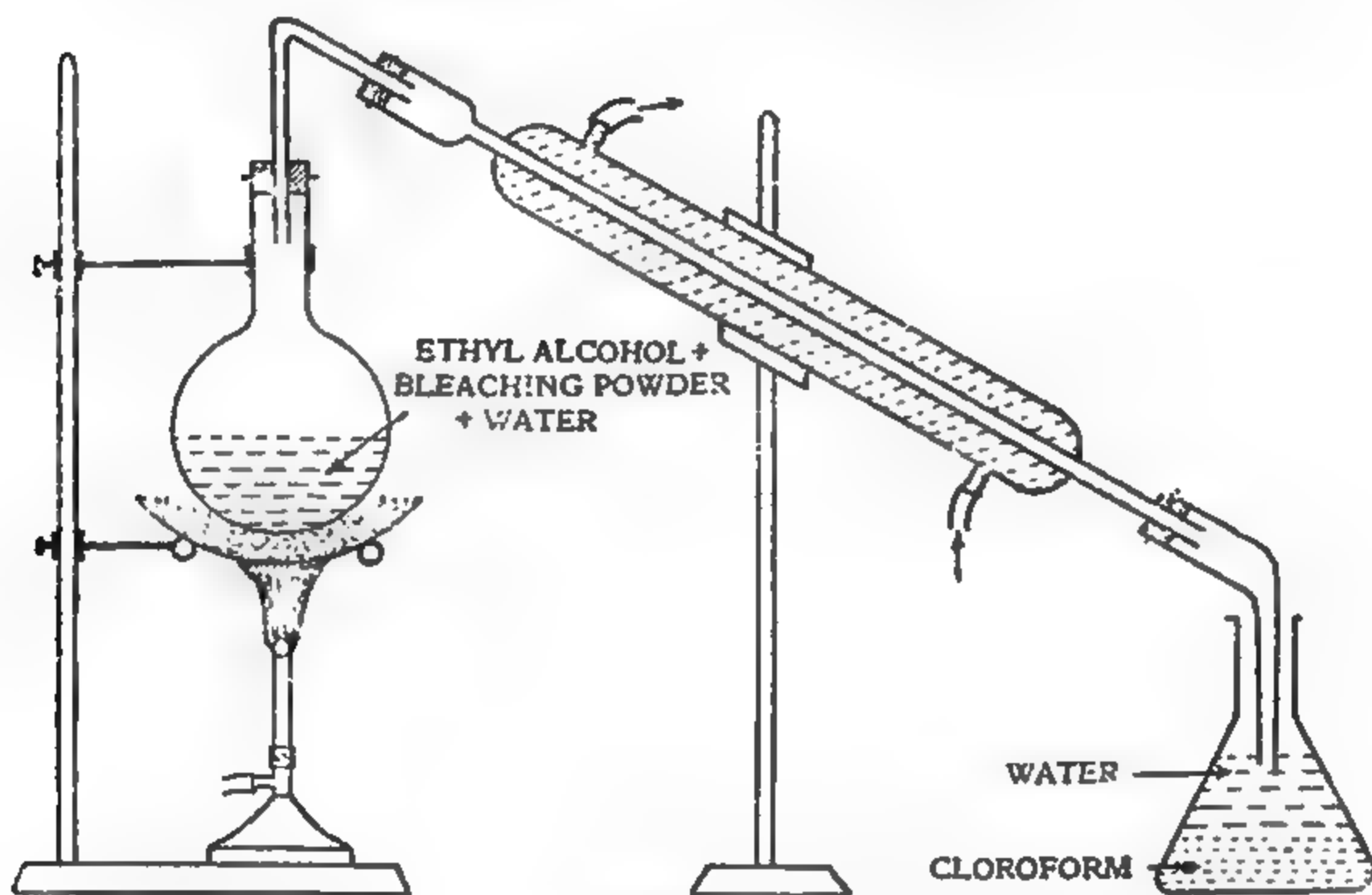
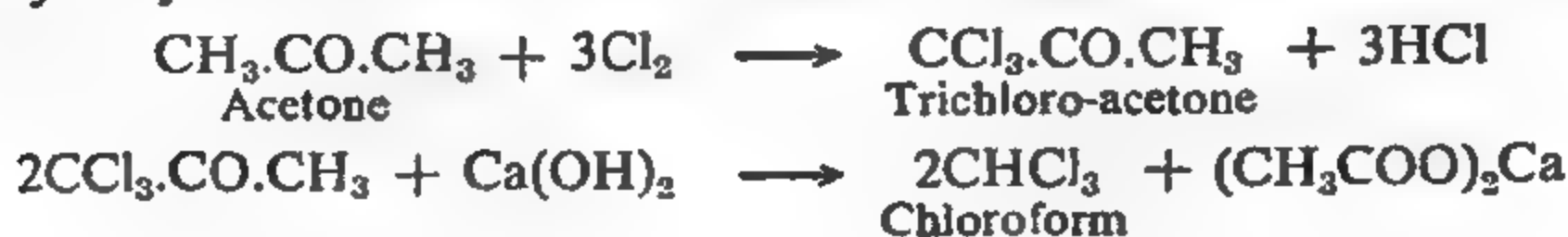


Fig. 2. Preparation of Chloroform.

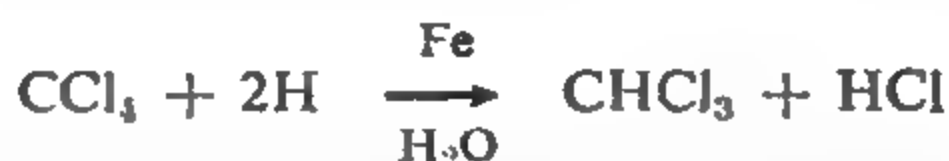
Laboratory preparation. The apparatus used for the laboratory preparation of chloroform is shown in Fig. 2.

About 100 gm. of bleaching powder is rubbed with about 400 ml. of water so as to get a thin paste of the material which is transferred to a two-litre round-bottom flask fitted with a condenser, an adapter and a receiver as shown. 25 ml. of alcohol or acetone is now added to the flask which is heated gradually on a sand bath. The distillate contains a mixture of water and chloroform which is separated by a separating funnel. The chloroform layer is washed with dilute alkali, dried over anhydrous calcium chloride and then redistilled. The fraction passing over between 60° – 65° is collected.

2. *Pure chloroform* can be obtained by the action of aqueous alkali on chloral hydrate.



3. In the U.S.A., chloroform is now *manufactured* by the reduction of carbon tetrachloride with iron filings and water or with iron and dilute acid.

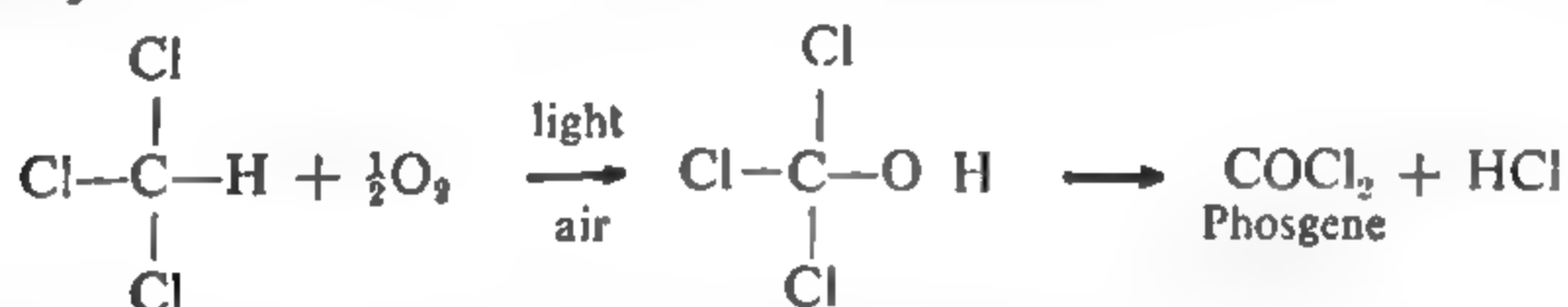


But the chloroform so obtained is *not pure* and is used only for *solvent purposes* and not as an anaesthetic.

Physical Properties. Chloroform is a colourless liquid (b.p. 61°) with a peculiar sickly sweet smell and sweetish taste. It is sparingly soluble in water but dissolves readily in alcohol and ether. It is a very good solvent for many organic substances such as oils, fats, resins, etc. Under usual conditions it is not combustible but its vapour may be ignited which burn with a green-edged flame. Chloroform vapours when inhaled, produce senselessness hence it is used as a general anaesthetic.

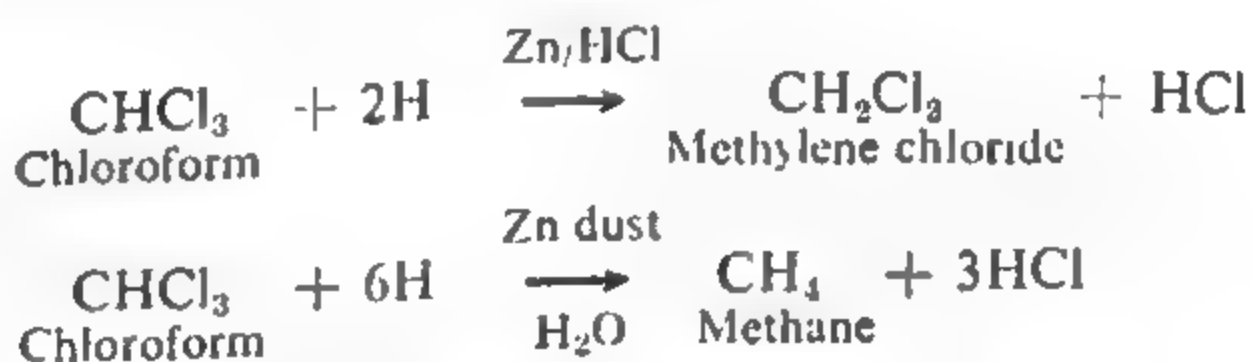
Chemical Properties. The important reactions of chloroform are :

(1) **Oxidation** In the presence of *air and light*, chloroform slowly decomposes into hydrogen chloride and the very poisonous phosgene, COCl_2 .



To avoid the formation of phosgene, the chloroform meant for anaesthetic purposes is stored in well-stoppered, dark blue or brown bottles. The addition of 1 per cent of ethyl alcohol is known to retard this decomposition.

(2) **Reduction.** When reduced with *zinc and hydrochloric acid*, methylene chloride is obtained while on reduction with *zinc dust and water*, methane is obtained.



(3) **Chlorination.** When treated with chlorine in the *presence of sunlight*, carbon tetrachloride is formed.

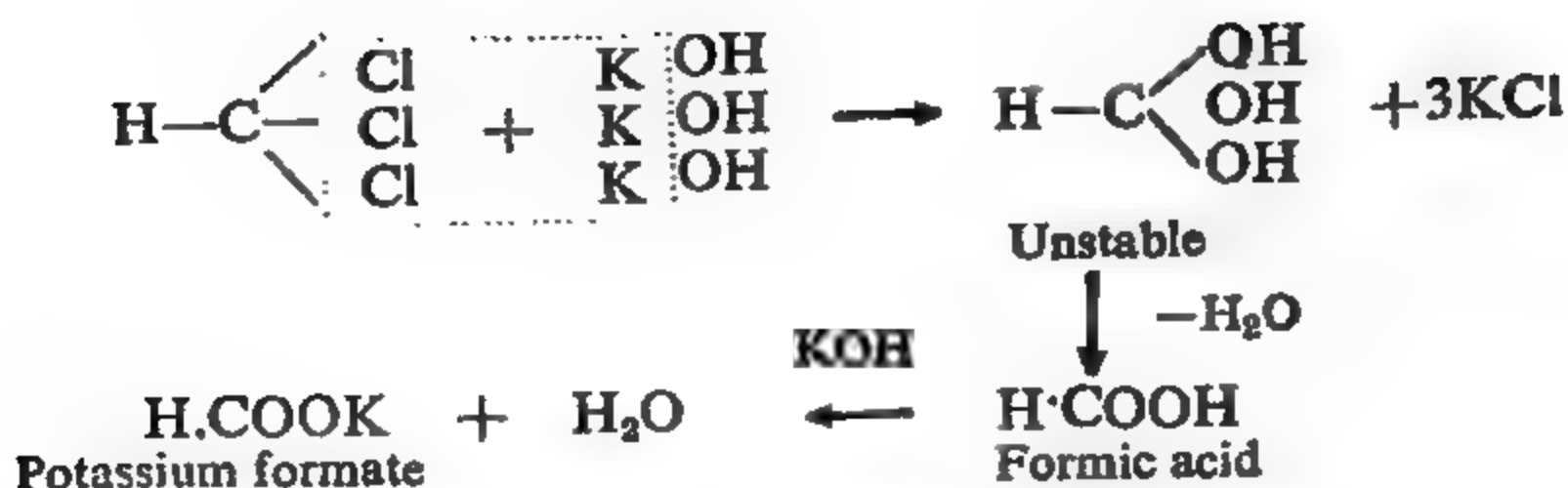


(4) **Nitration.** When treated with *concentrated nitric acid*, chloroform gives *chloropicrin* (nitrochloroform).

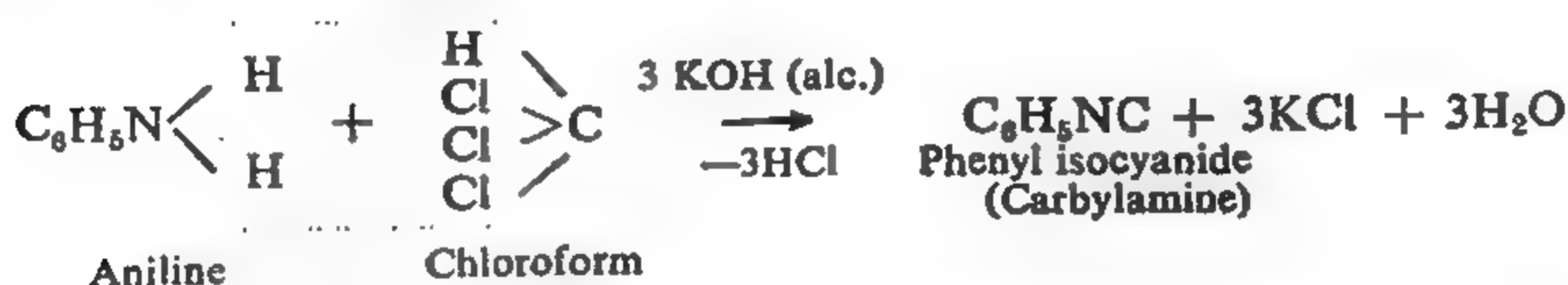


Chloropicrin is a *poisonous liquid* (b.p. 112°) and is used as an insecticide.

(5) **Hydrolysis.** When heated with *concentrated aqueous or alcoholic potash*, chloroform is hydrolysed to give potassium formate.



(6) **Carbylamine reaction.** When warmed with *aniline and alcoholic potash*, chloroform gives phenyl isocyanide or *carbylamine* which has an extremely disagreeable nauseating odour.



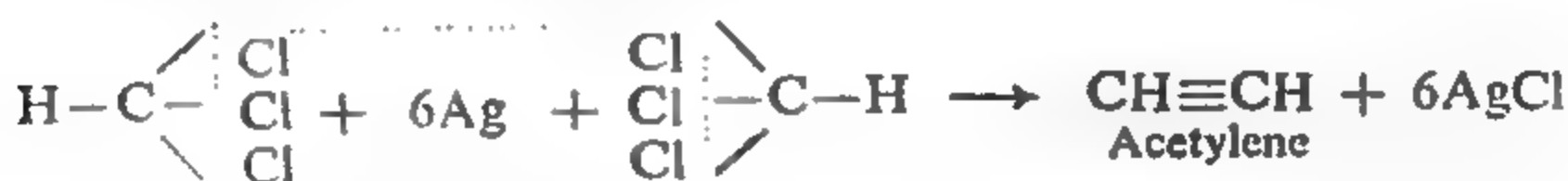
This reaction is used as a **delicate qualitative test** for chloroform.

Instead of aniline, any primary amine (R—NH₂) can be used and hence this reaction is also employed as a *test for primary amines*.

(7) **Condensation with acetone.** Chloroform readily condenses with acetone in the presence of potassium hydroxide, giving *chloretone* which is used as a hypnotic, particularly against sea sickness.



(8) **Dehalogenation.** When warmed with *silver powder*, chloroform loses six chlorines from two molecules, giving acetylene.



Uses . Chloroform is used :

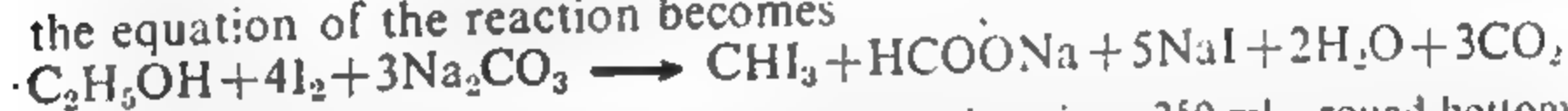
- (1) In industry as a solvent for fats, waxes, resins, rubber, etc.
- (2) As a general anaesthetic. (Since chloroform has a strong tendency to inhibit the action of the heart, it is being replaced by other anaesthetics.
- (3) As a preservative for animal or vegetable infusions or decoctions.
- (4) As a laboratory reagent for testing the presence of primary amines.
- (5) Chloroform also finds extensive use in medicine.

Iodoform, Tri-iodomethane, CHI_3

Laboratory Preparation. Iodoform is prepared in laboratory by the action of iodine and alkali upon ethyl alcohol or acetone. The mechanism of the reaction is the same as in the case of chloroform, viz.,



Sodium carbonate can also be used in place of sodium hydroxide when the equation of the reaction becomes



Details. 15 gm. of sodium carbonate is taken in a 250 ml. round bottomed flask and 50 ml. of water added to it. Sodium carbonate is dissolved by shaking. 10 ml. of alcohol is then added and the mixture well shaken. Further, 5 gm. of iodine is added gradually by continuous shaking. The flask is then heated on a water bath to about 70° , till the colour of iodine is discharged. On cooling, yellow crystals of iodoform separate out. These are filtered, washed with water and recrystallised from alcohol.

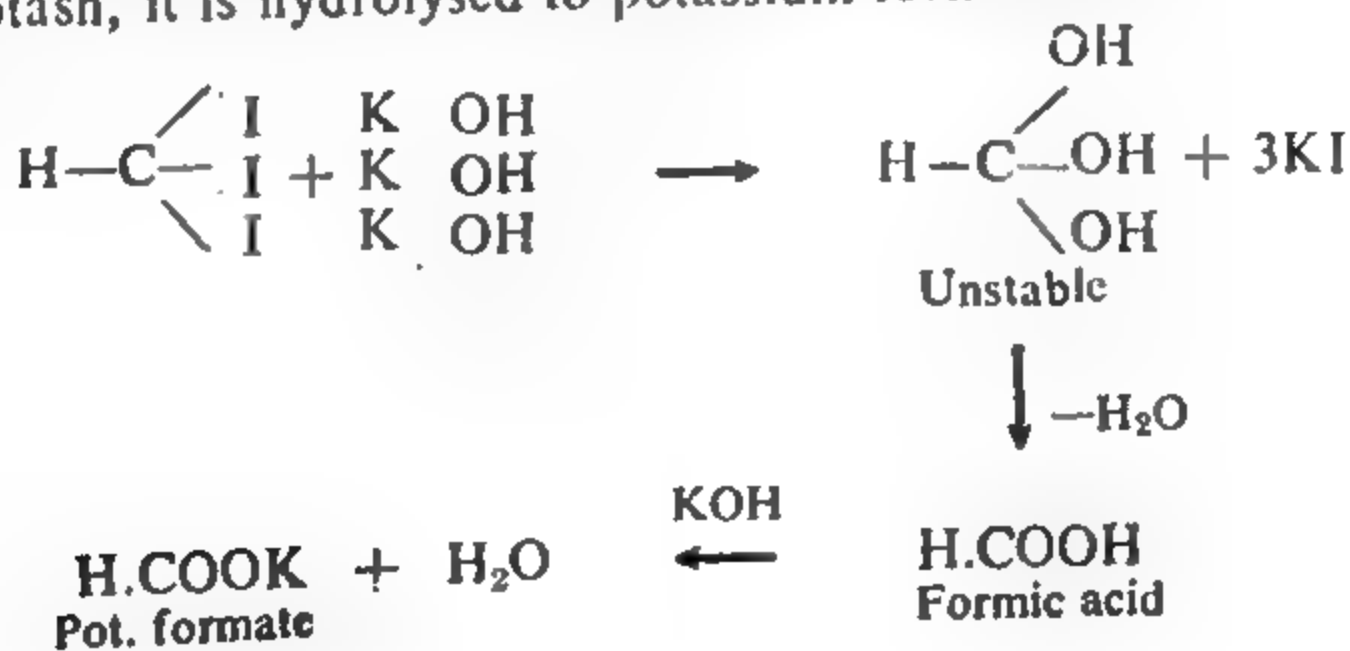
Commercial Preparation. On a commercial scale, iodoform is now prepared by the electrolysis of an aqueous solution of ethyl alcohol containing sodium carbonate and potassium iodide. The solution is maintained at 70° . During electrolysis, iodine is set free at the anode and potassium hydroxide is formed at the cathode. This is neutralized by passing gaseous carbon dioxide.

The iodine liberated reacts with ethyl alcohol in the presence of sodium carbonate to form iodoform.

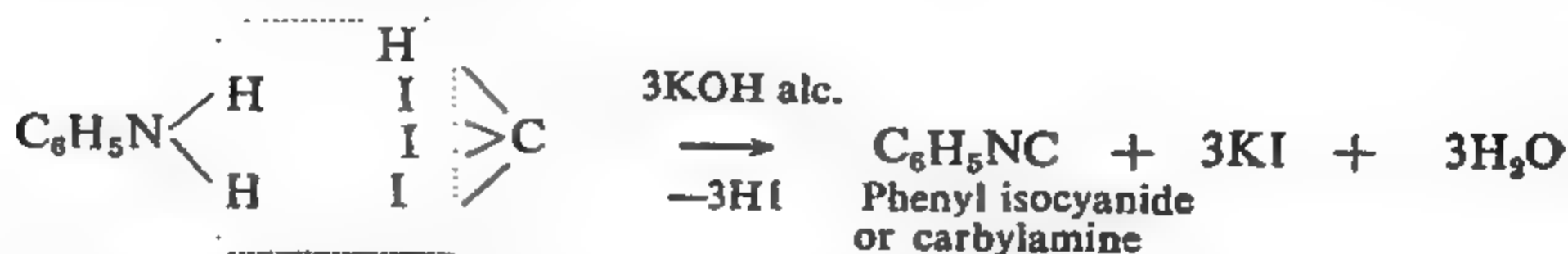
Physical Properties. Iodoform crystallises in lustrous, yellow hexagonal plates, having a characteristic strong smell. Its melting point is 112° . It is insoluble in water but is readily soluble in alcohol, chloroform and ether.

Chemical Properties. In chemical properties it resembles chloroform and gives almost the same reactions. For example,

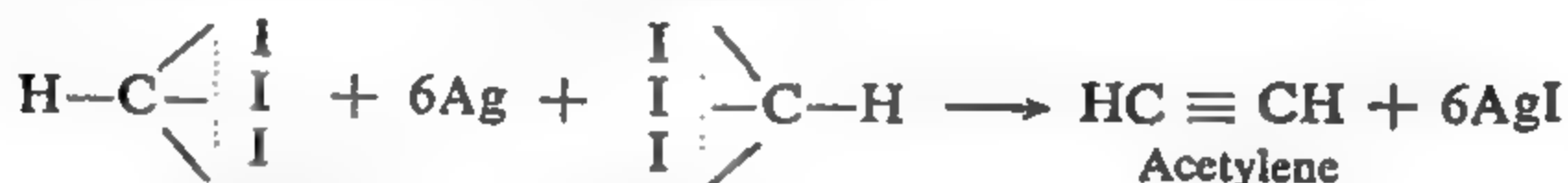
(1) **Hydrolysis.** When boiled with alcoholic or aqueous solution of caustic potash, it is hydrolysed to potassium formate.



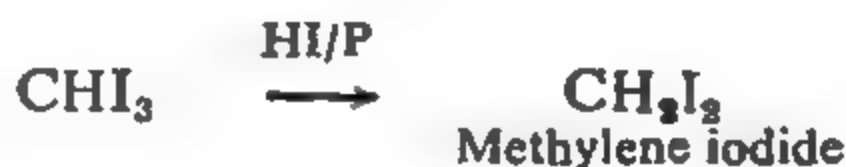
(2) **Carbylamine reaction.** When warmed with aniline and alcoholic potash it gives phenyl isocyanide or *carbylamine* which has an extremely disagreeable nauseating smell.



(3) **Dehalogenation.** When warmed with silver powder, iodoform loses six atoms of iodine from two molecules, giving acetylene.



(4) **Reduction.** On reduction with HI and red phosphorus, it gives methylene iodide.



Uses. Iodoform is extensively used as an antiseptic for dressing wounds. Its antiseptic properties are due to the liberation of iodine when it comes in contact with organic matter and *not* to iodoform itself.

TETRA-HALOGEN DERIVATIVES

Carbon Tetrachloride, CCl_4

Preparation. Carbon tetrachloride is prepared on a commercial scale by the following methods :

(1) By the chlorination of carbon disulphide in the presence of aluminium chloride (or antimony pentachloride or ferric chloride,) which acts as catalyst or halogen carrier.



The sulphur monochloride (b.p. 138°) is separated by fractional distillation, and reacted with a further quantity of carbon disulphide to yield carbon tetrachloride.



The carbon tetrachloride fraction is then shaken with sodium hydroxide and finally distilled to get pure carbon tetrachloride.

(2) By the chlorination of natural gas (methane) in the presence of partly reduced cupric chloride (catalyst) using a proper ratio of chlorine to methane.



(3) *By chlorinolysis of propane.* Chlorinolysis is the process of chlorinating an organic compound under such conditions as result in the cleavage of the carbon-carbon bond to give chloro compounds with lesser number of carbon atoms than the original compound.

Thus, propane when heated with chlorine at 300° – 400° under a pressure of about 70 atmospheres yields a mixture of carbon tetrachloride and hexa chloro-ethane.

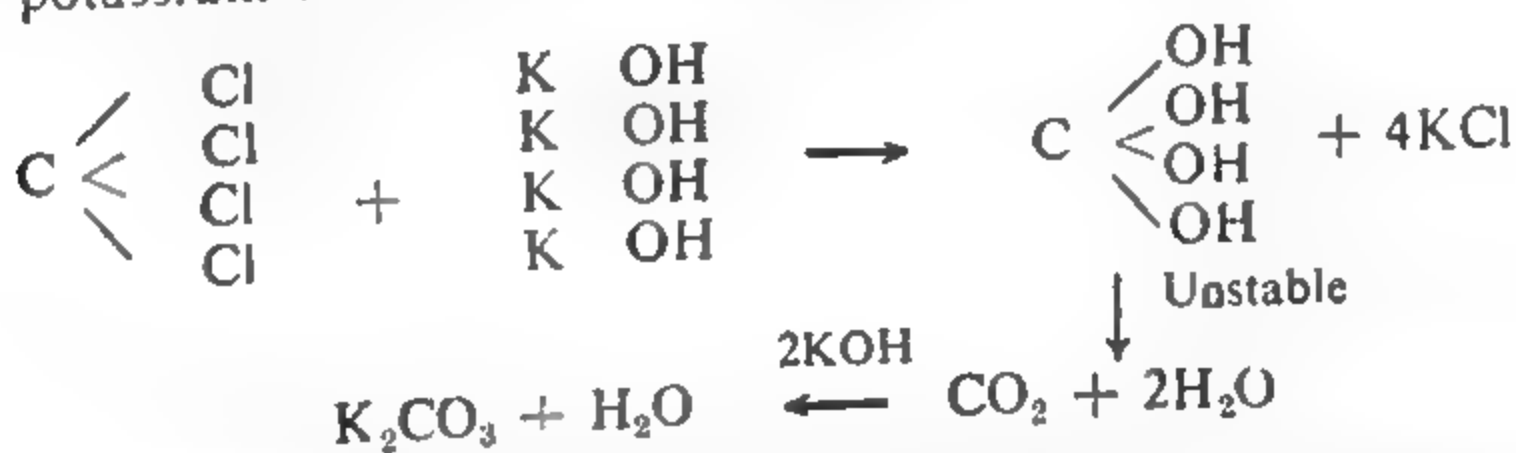


hexa chloro-ethane is a solid substance and can be easily separated.

Physical Properties. Carbon tetrachloride is a colourless liquid (b.p. 77°) with a sickly smell. It is insoluble in water but is freely miscible with organic solvents such as ether, ethyl alcohol, etc. It is an excellent solvent for oils and fats.

Chemical Properties. Carbon tetrachloride is comparatively inert and gives only a few reactions such as :

(1) **Hydrolysis.** When heated with alcoholic potash, it is hydrolysed to give potassium carbonate and potassium chloride.



(2) **Reduction.** It is reduced to chloroform by moist iron filings.



(3) **Oxidation.** Carbon tetrachloride is stable even at red heat (500°). But in the presence of water vapour at this high temperature, it is partially oxidised to phosgene.



Uses. (1) Carbon tetrachloride readily produces dense, incombustible vapour, hence it is used as a fire extinguisher under the name pyrene. The liquid when sprayed on the fire produces a dense blanket of vapour between the burning material and air and thereby the fire is put out.

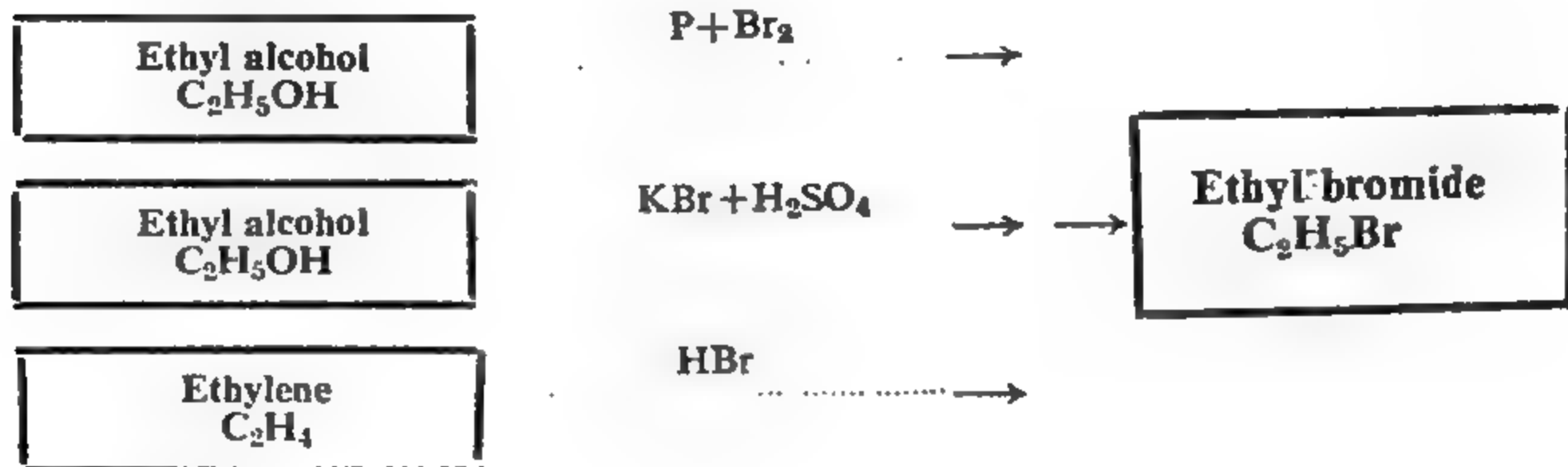
(2) Since the vapour of carbon tetrachloride are non-flammable, it is extensively used as an industrial solvent for fats, oils, resins, lacquers, etc.

(3) It is also used as a dry cleaning agent. It is a very effective cleaner for bath room tiles, car parts, stoves, etc.

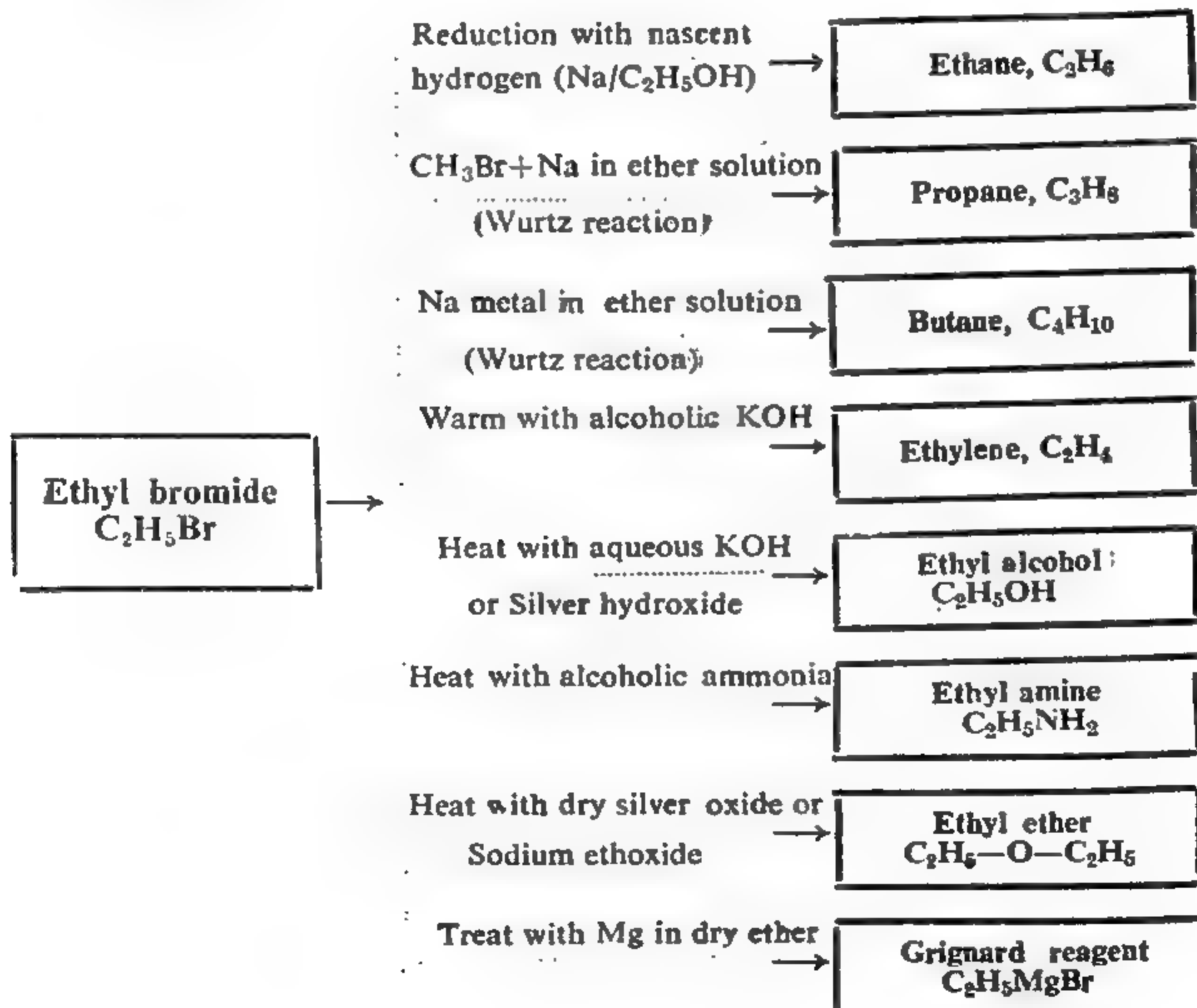
(4) It is used as an insecticide and also as an anti-hookworm medicine.

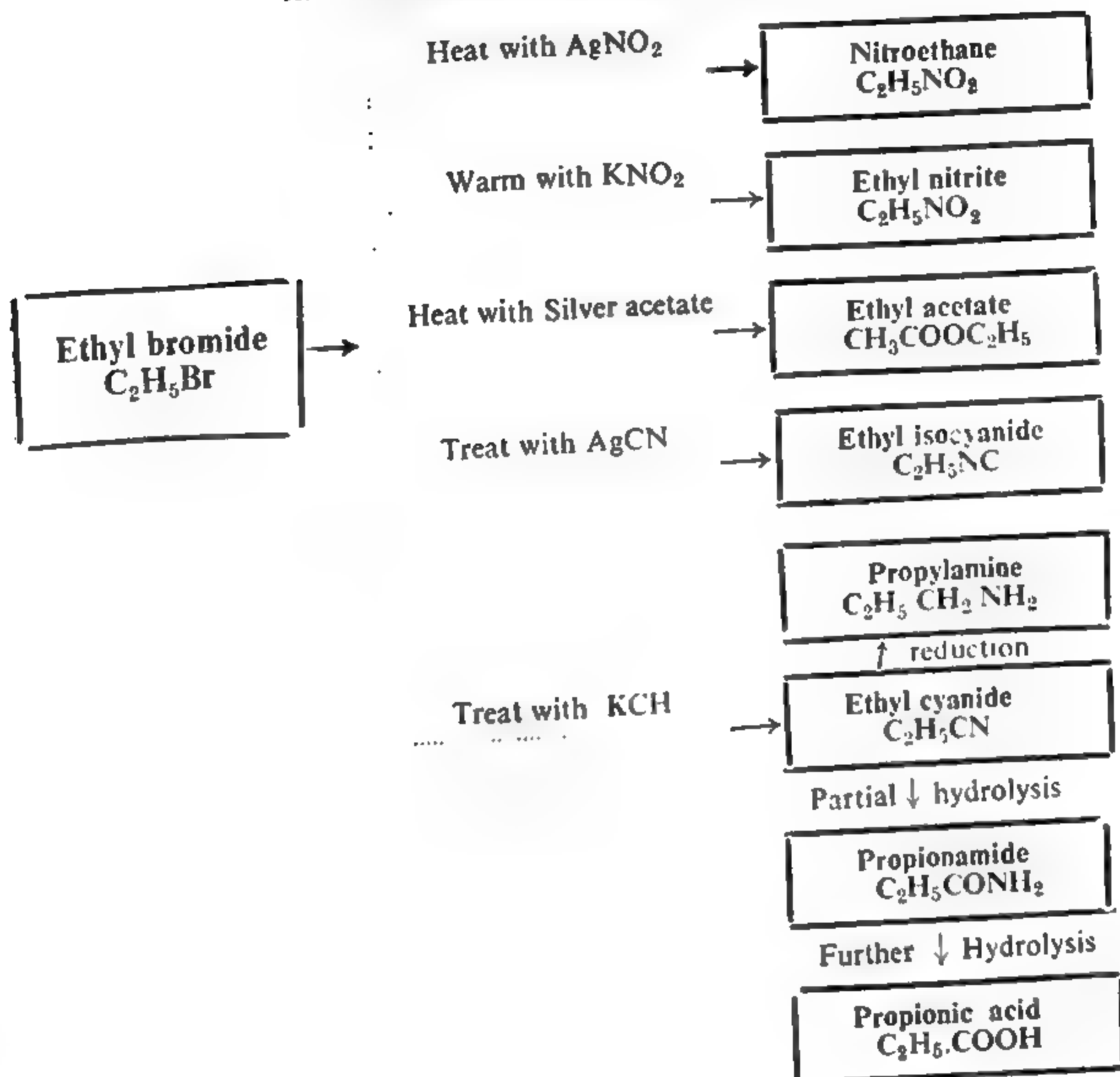
SUMMARY OF TYPICAL MEMBERS

Preparation.

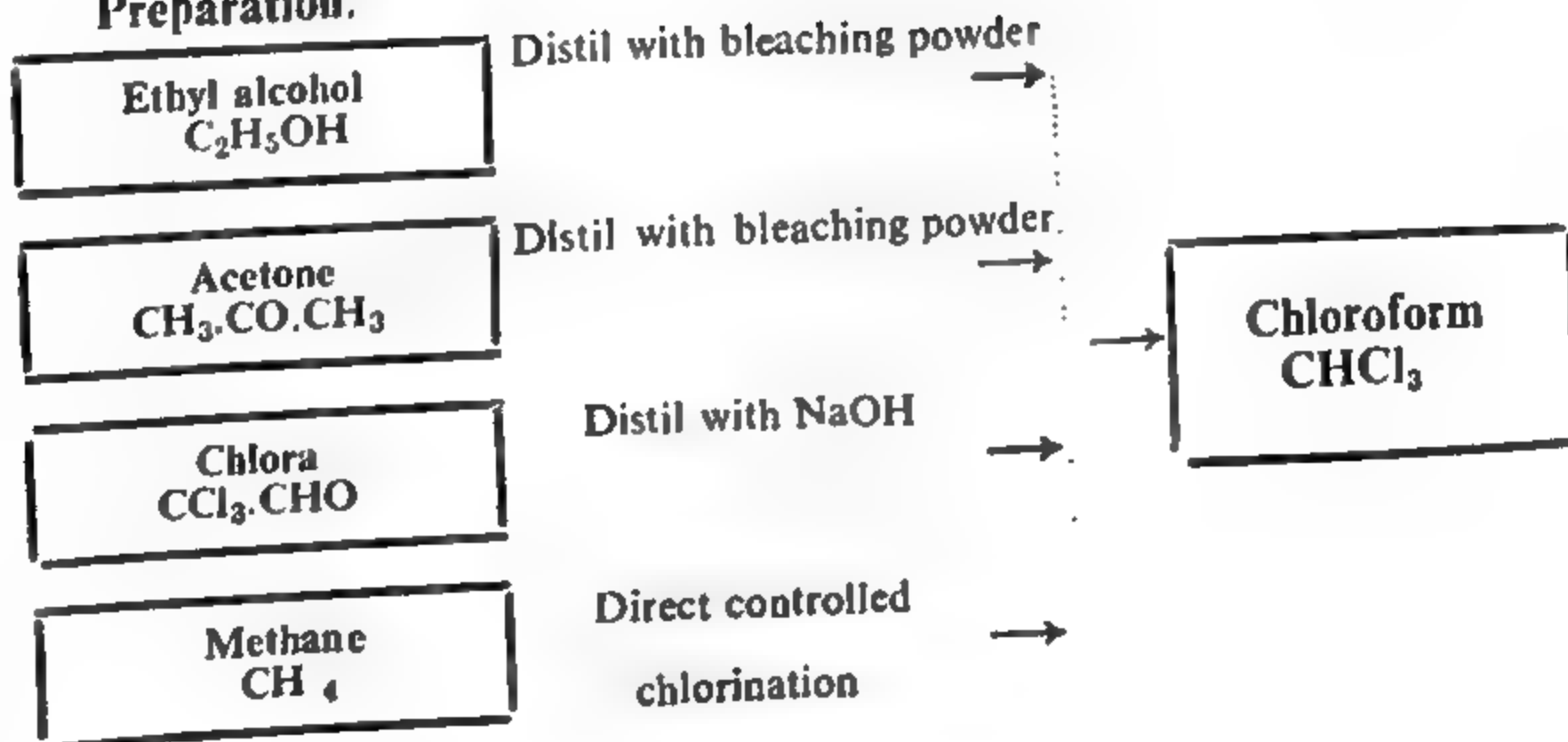


Properties.

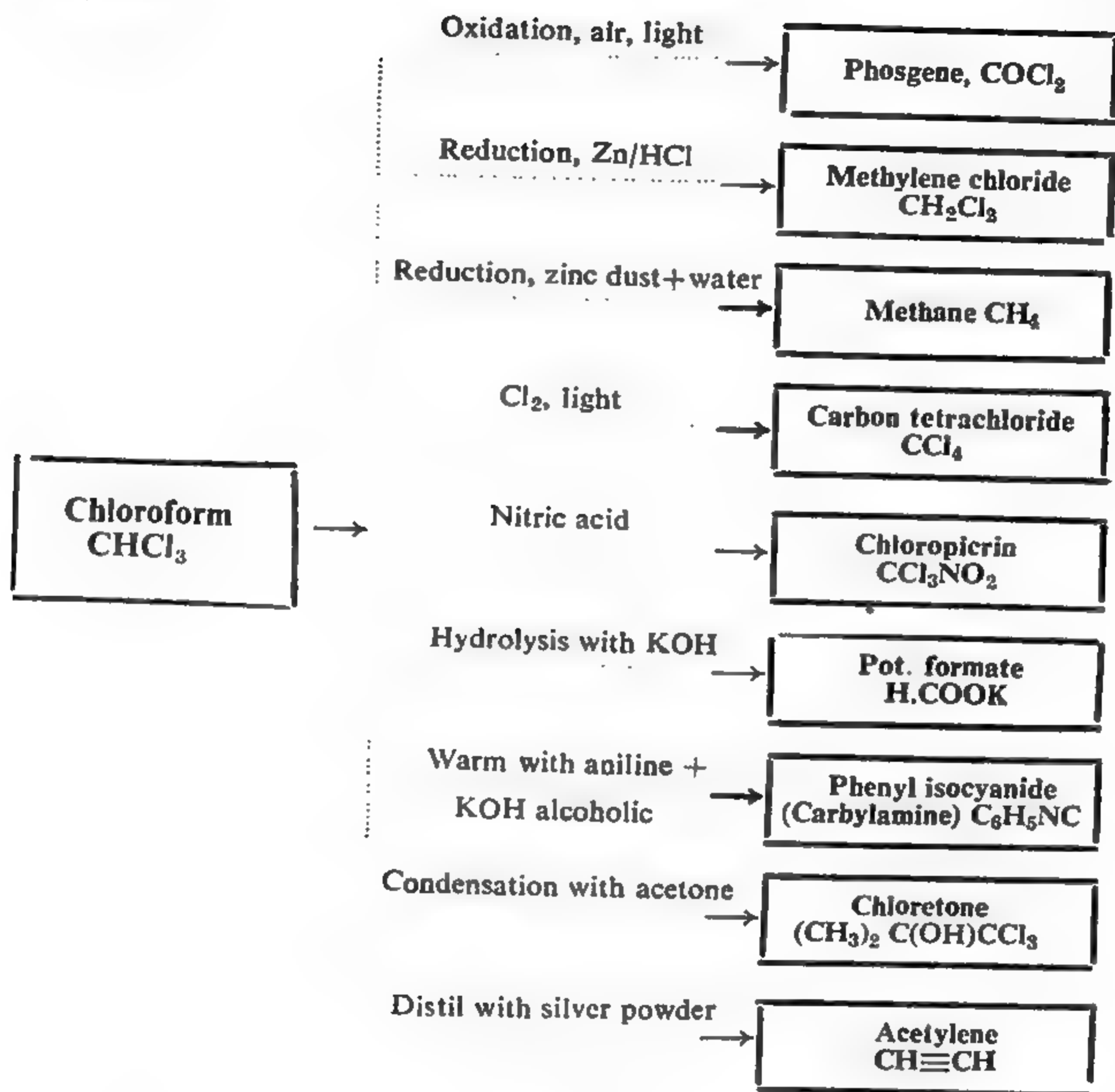




Preparation.



Properties.



QUESTIONS

1. What are halogen derivatives of alkanes ? How are they classified ?
2. What are alkyl halides ? How are they produced ? Give their reactions.
3. How is ethyl bromide prepared in the laboratory ? How can it be converted into (i) Ethane (ii) Propane (iii) Ethylene (iv) Ethyl alcohol (v) Ethyl ether (vi) Ethylamine (vii) Ethyl acetate.
4. How is ethyl chloride prepared in the laboratory ? Give its important synthetic reactions.
5. Give an account of the preparation, properties and uses of ethyl iodide.
6. How is chloroform prepared in the laboratory ? Give its important properties and uses.
7. Explain giving reactions and experimental details how ethyl alcohol can be converted into trichloromethane. Give the important properties and uses of trichloromethane.
8. Give the laboratory preparation of chloroform. How can it be converted into (i) Methane (ii) Carbon tetrachloride (iii) Formic acid (iv) Phosgene (v) Phenyl isocyanide and (vi) Nitrochloroform

9. Give the laboratory preparation of iodoform. Describe its important properties and uses.
10. Describe the manufacture of carbon tetrachloride. Give the important reactions and uses of the compound.
11. Describe the preparation, properties and uses of trichloromethane. *(Panjab Inter 1956)*
12. Give two methods of preparing methyl chloride and describe general reactions of alkyl halides. *(Panjab Inter 1961 Suppl.)*
13. With an alkyl halide as a starting material how will you proceed to obtain
(i) A paraffin (ii) Acetamide (iii) Nitroethane (iv) Ethyl acetate? *(Panjab Inter 1959)*
14. (a) Describe a laboratory method for preparing a pure sample of iodoform. Explain the various reactions involved with the help of chemical equations.
(b) State four important properties of chloroform; represent each one by a chemical equation and name the main product formed. *(Panjab Inter 1958)*
15. Give a method of preparing a specimen of ethyl bromide. What reactions it undergoes with.
(a) Aqueous potassium hydroxide.
(b) Sodium ethoxide.
(c) Sodium.
16. "Aliphatic monohalogen derivatives can form the starting point for obtaining a large variety of organic compounds". Amplify the statement with illustrations. *(Panjab Inter 1958)*
17. Give the preparation, properties and uses of iodoform. How does it differ from chloroform?
18. "Aliphatic mono-halogen derivatives form a powerful synthetic instrument in the hands of an organic chemist." Justify this statement. *(Panjab Inter 1952 Suppl.)*
19. "A just selection of an alkyl halide can be utilised for the synthesis of a desired aliphatic compound." Discuss the above statement illustratively. *(Panjab Inter 1950, 63)*
20. Give the preparation, properties and uses of a liquid trihalogen derivative of methane. *(Panjab Inter 1951)*
21. "The aliphatic halogen compounds are amongst the most reactive of all organic compounds." Illustrate this statement. *(Panjab Inter 1958)*
22. Two isomeric compounds having the composition $C_2H_4Cl_2$ are known. How are these compounds obtained, and their constitution been determined? *(Panjab Inter 1955)*
23. How is chloroform prepared on laboratory scale? What happens when it is acted upon by (a) Chlorine (b) NaOH (c) Sodium hydroxide and aniline. Mention the uses of chloroform. *(Panjab Inter 1947)*
24. Fill in the blanks :
(i) Direct iodination of alkane is not possible because—produced acts as a reducing agent.
(ii) An alkyl halide when treated with—yields an alcohol.
(iii) —is obtained when—is treated with alcoholic potash.
(iv) An alkyl halide reacts with potassium cyanide to give—which can be used to produce—and—
(v) Chloroform reacts with a primary amine in the presence of —to yield —which has an extremely unpleasant odour.
(vi) Chloroform required for anaesthetic purposes is kept in —bottles and about 1% —is added so that the harmful—is destroyed.
(vii) Alkyl halides react with alcoholic ammonia to yield a mixture of —
(viii) The two types of dihalogen derivatives are — and —
(ix) Esters are formed when alkyl halides react with —
(x) —react with Mg in dry ether to yield—which are very important synthetic reagents.

CHAPTER XXXI

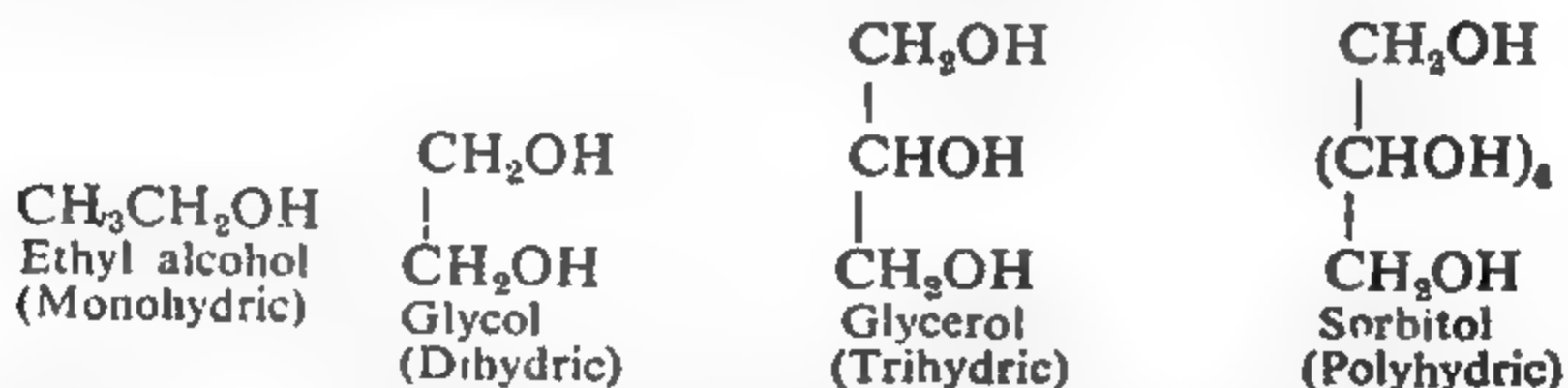
ALCOHOLS

An alcohol is a compound obtained by replacing one or more hydrogen atoms of a hydrocarbon by one or more hydroxyl(OH) groups. In other words, *alcohols are the hydroxy derivatives of hydrocarbons*. They may also be considered as *alkyl derivatives of water*.



Similarities of alcohols to both the parent substances exist. The lower members, in which the hydroxyl group constitutes a considerable part of the total molecule, behave like water while the higher members, in which the hydrocarbon radical outweighs the hydroxyl group, bear more resemblance to the hydrocarbons.

The alcohols are classified as **mono—,di—or trihydric** alcohols according as the number of hydroxyl groups present in their molecule is one, two or three respectively. When they contain four or more hydroxyl groups, they are termed as **polyhydric** alcohols. For example,

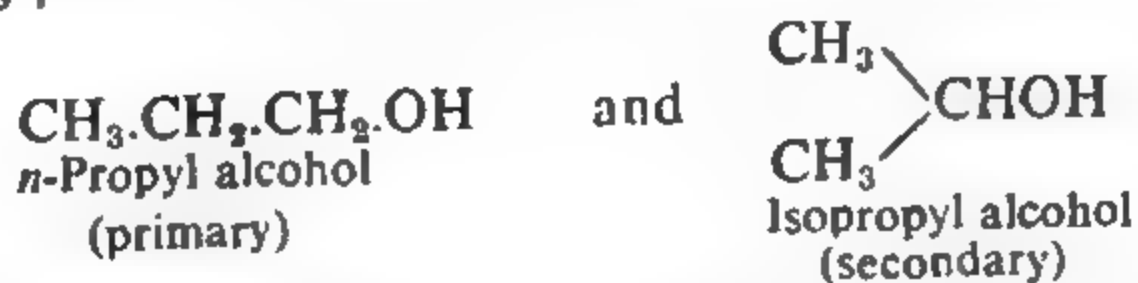


Monohydric Alcohols. As mentioned above, the monohydric alcohols are those which contain only one hydroxyl group. They form a homologous series with the general formula $\text{C}_n\text{H}_{2n+1}.\text{OH}$, usually represented as R.OH where R is the alkyl radical (methyl, ethyl, propyl, etc.) For example,

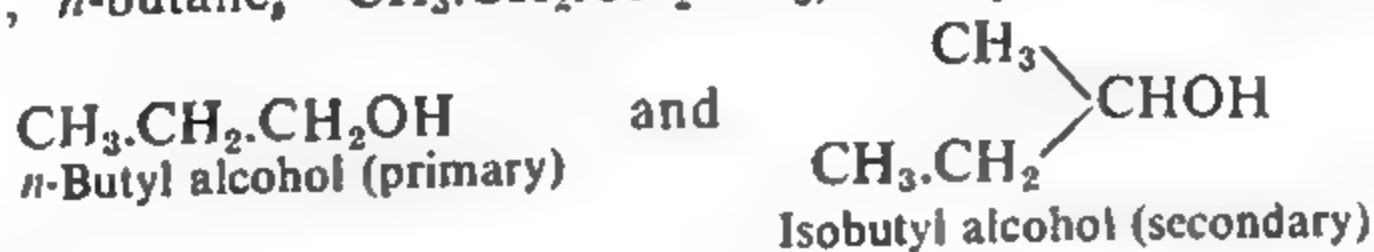


The monohydric alcohols are further subdivided into **primary, secondary** and **tertiary** alcohols according as the hydroxyl group is attached to a primary, a secondary or a tertiary carbon atom. For example, the end carbon atoms in *n*-propane, $\text{CH}_3\text{CH}_2\text{CH}_3$, are primary, whereas the

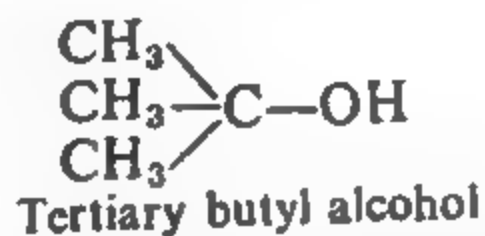
central carbon atom is secondary. Therefore, *n*-propane can give rise to two alcohols :



Similarly, *n*-butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, can yield two alcohols :



Isobutane, $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \\ \diagup \\ \text{CH}_3 \end{array} \text{CH}_2\text{CH}_3$, in addition to a primary alcohol, also gives a tertiary alcohol,



It will be noted that primary, secondary and tertiary butyl alcohols, mentioned above, are all isomeric with one another as they have the same molecular formula, $\text{C}_4\text{H}_{10}\text{O}$.

Thus, the characteristic groups of primary, secondary and tertiary alcohols, respectively, are



Nomenclature. There are three systems of naming the alcohols :

(1) *Common System.* In this system, the name of alcohol is derived by adding the word alcohol after the name of the alkyl group present in the molecule. Thus, $\text{C}_2\text{H}_5\text{OH}$ is ethyl alcohol and

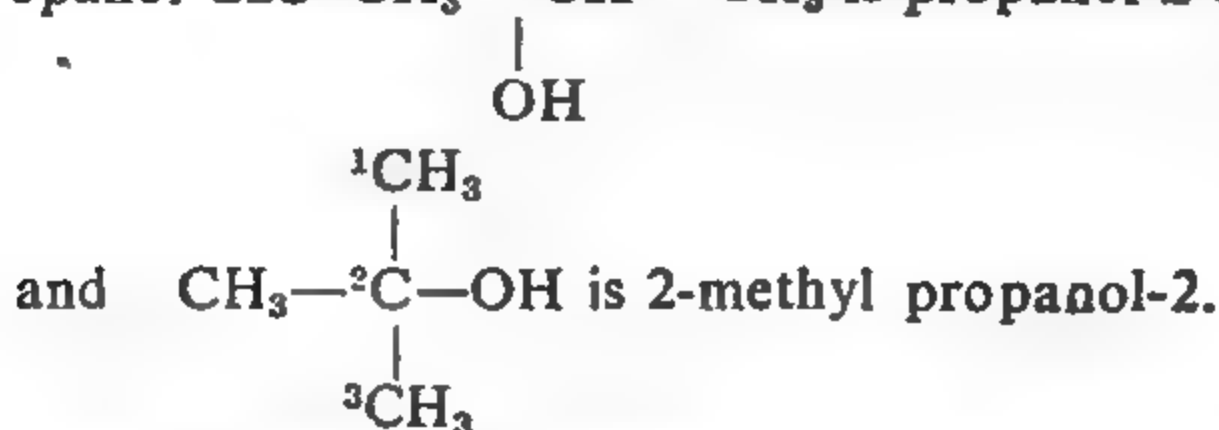


(2) *Derived System.* In this system, the alcohol is considered to be a derivative of methyl alcohol, which is called 'carbinol'.

Thus, $\text{CH}_3\text{CH}_2\text{OH}$ is methyl carbinol and $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \\ \diagup \\ \text{CH}_3 \end{array} \text{CHOH}$ is dimethyl carbinol.

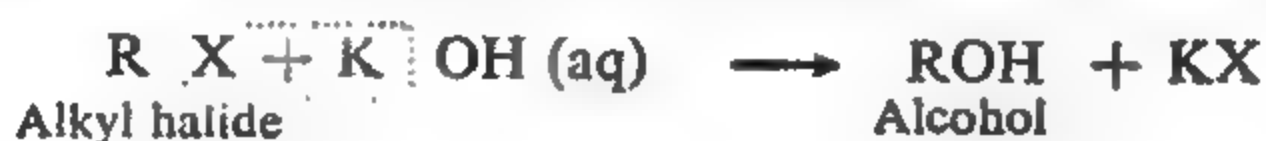
(3) *I. U. C. System.* In this system, the suffix -e of the name of the corresponding alkane is changed to -ol and the position of the hydroxyl group is indicated by a numeral added before or after the name of the parent alkane. Thus, ${}^3\text{CH}_3\text{.}{}^2\text{CH}_2\text{.}{}^1\text{CH}_2\text{OH}$ is propanol-1 or

1-propanol and $^3\text{CH}_3\text{—}^2\text{CH—}^1\text{CH}_3$ is propanol-2 or 2-propanol



General Methods of Preparation. Monohydric alcohols can be prepared by the following general methods :

(1) **By the hydrolysis of alkyl halides.** Alkyl halides when boiled with an aqueous solution of an alkali hydroxide yield alcohols.



For example,



This method, however, is *not very satisfactory* because the alkyl halides simultaneously lose a molecule of hydrogen halide forming olefins. Hence, alkali hydroxide is usually replaced by *mild alkalies* such as moist silver oxide or aqueous potassium carbonate.



(2) **By the hydrolysis of esters.** On heating with a dilute solution of an alkali, the esters get hydrolysed to give alcohols.

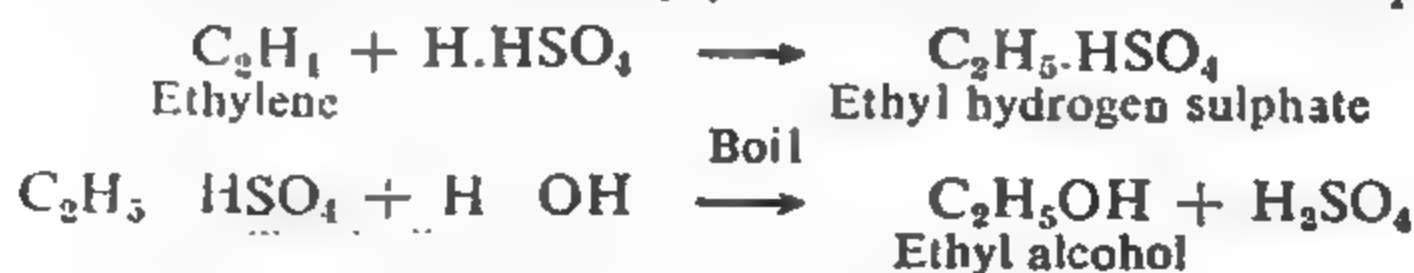


For example,



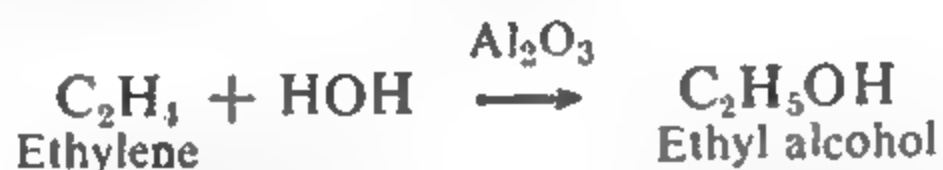
This method is employed industrially for the preparation of higher alcohols from natural esters such as bees wax, oils and fats.

(3) **By the hydration of olefins.** Olefins when passed into sulphuric acid are absorbed giving alkyl hydrogen sulphates which when boiled with water or treated with steam readily yield alcohols. For example,



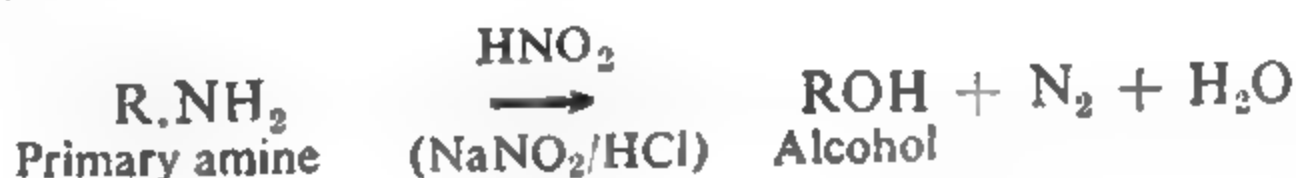
Thus, this method involves hydration of an olefin.

Direct hydration. It is now possible to carry out the direct hydration of olefins in the presence of catalysts to form alcohols. Thus, ethylene combines directly with water at *low temperatures* and *high pressures* in the presence of *catalysis* such as *aluminium oxide* or *barium acid phosphate* to yield ethyl alcohol.

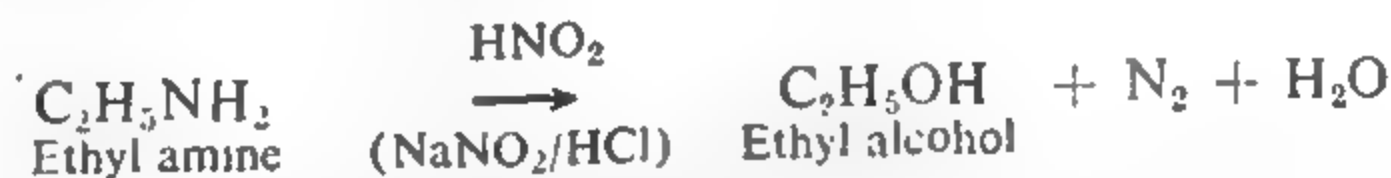


Large quantities of alcohol are now prepared by this method.

(4) **By the action of nitrous acid on primary amines.** Primary amines on treatment with nitrous acid (sodium nitrite + dilute mineral acid) yield alcohols.

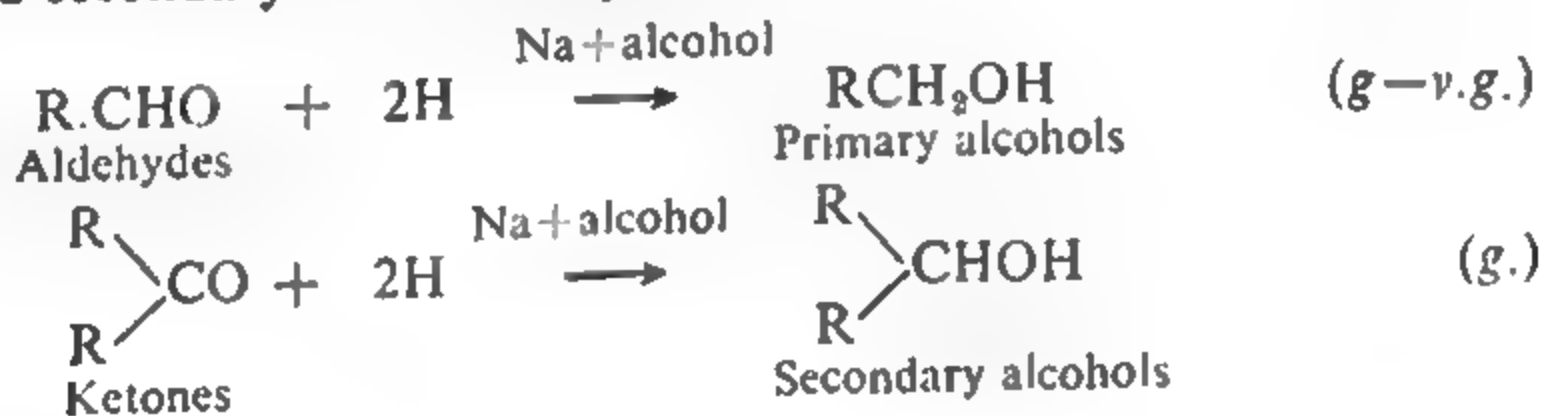


For example,

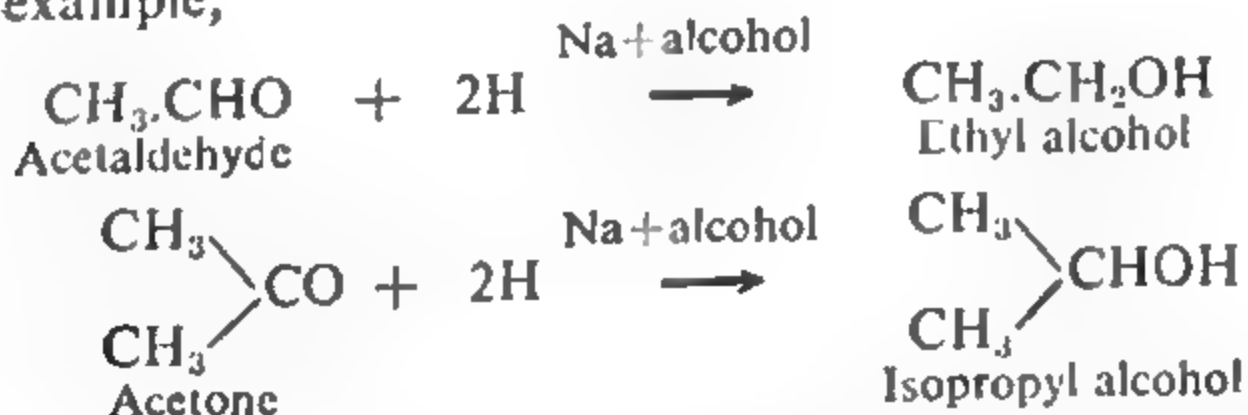


This reaction is not so simple and straight forward.

(5) **By the reduction of aldehydes and ketones.** Aldehydes and ketones, on treatment with excess of sodium and ethyl alcohol, are reduced to primary and secondary alcohols respectively.

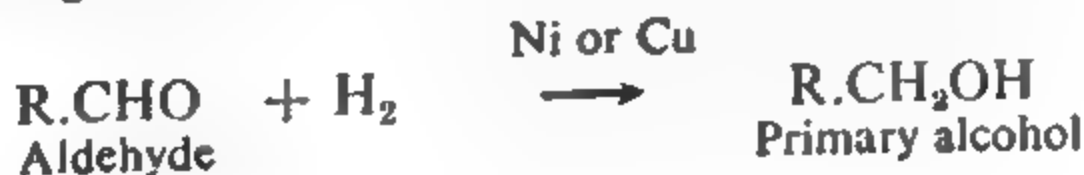


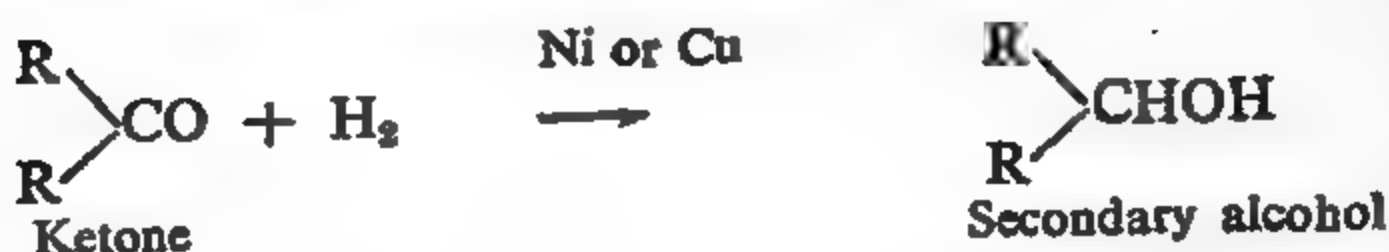
For example,



Recently, it has been shown that reduction with *sodium borohydride* (NaBH_4) and *lithium aluminium hydride* (LiAlH_4) in ether solution gives much better yield of alcohol than with sodium and alcohol.

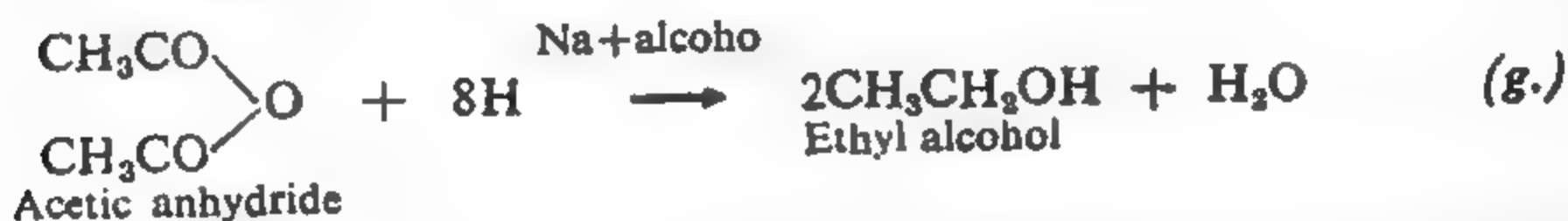
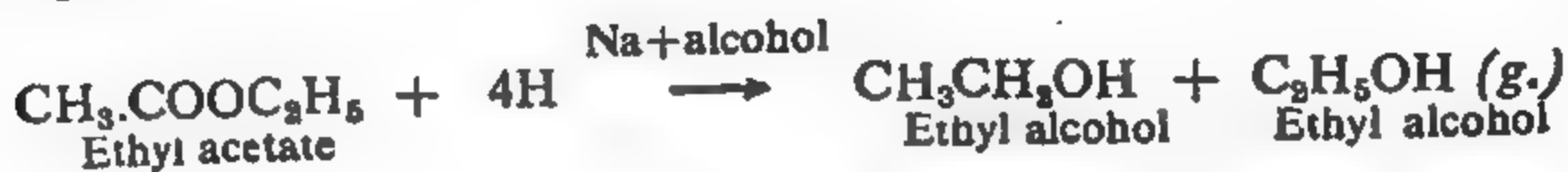
Catalytic reduction. Aldehydes and ketones can also be reduced catalytically to give alcohols. Nickel or copper is used as a catalyst.





(6) By the reduction of esters, acid chlorides, acid anhydrides and fatty acids.

(i) Esters of fatty acids, acid chlorides and acid anhydrides can be reduced to alcohols with *sodium metal and alcohol* or with *sodium hydride* or best with *lithium aluminium hydride* in ether solution. For example,

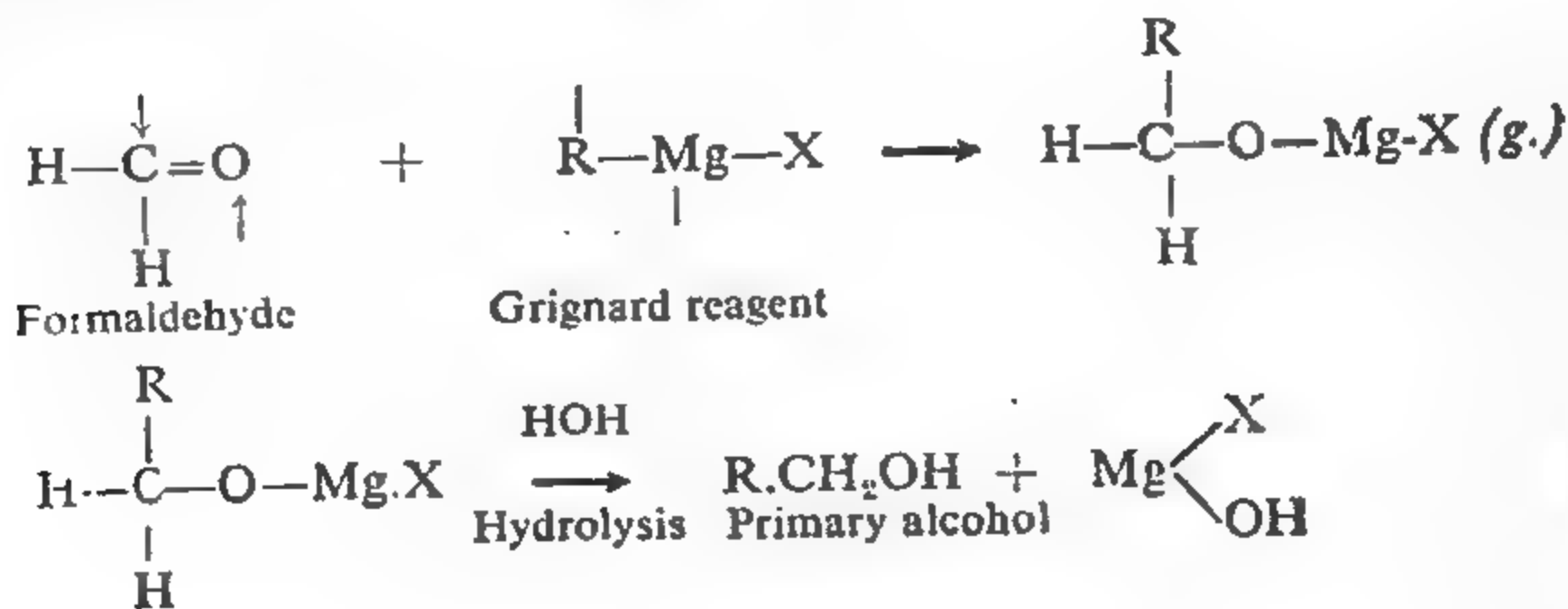


(ii) Reduction of esters, acid chlorides and acid anhydrides can also be carried out with hydrogen in the presence of a metal catalyst (copper or nickel) at 200° under a pressure of 150–200 atmospheres. Catalytic reduction is particularly useful for getting higher alcohols from natural esters.

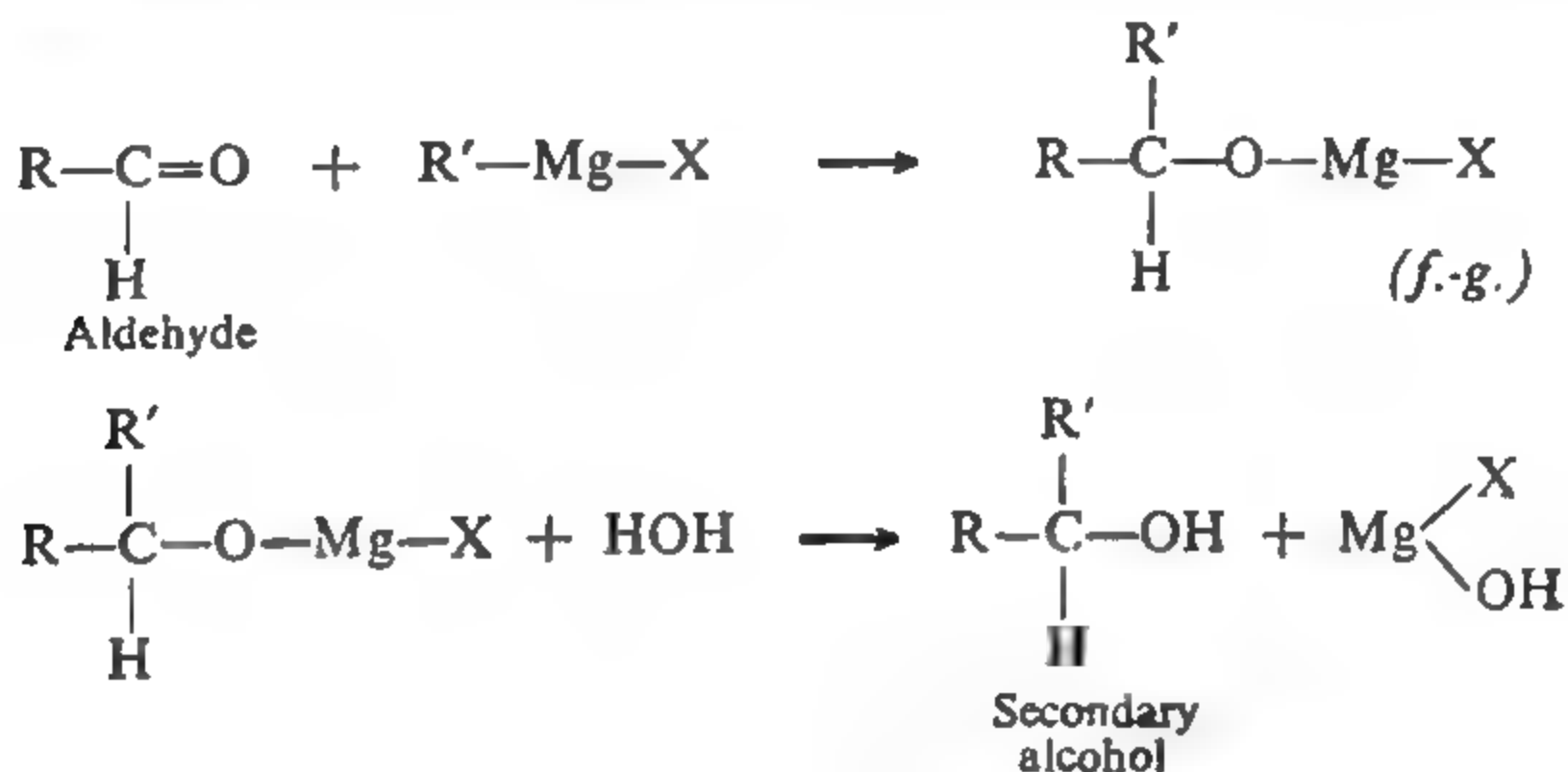
(iii) Recently (1955) it has been shown that carboxylic acids can also be reduced *directly* to alcohols by hydrogen in the presence of a *ruthenium* or *copper chromite* catalyst.

(7) From Grignard reagents. All the three types of alcohols (*viz.*, primary, secondary and tertiary) can be readily obtained from Grignard's Reagents.

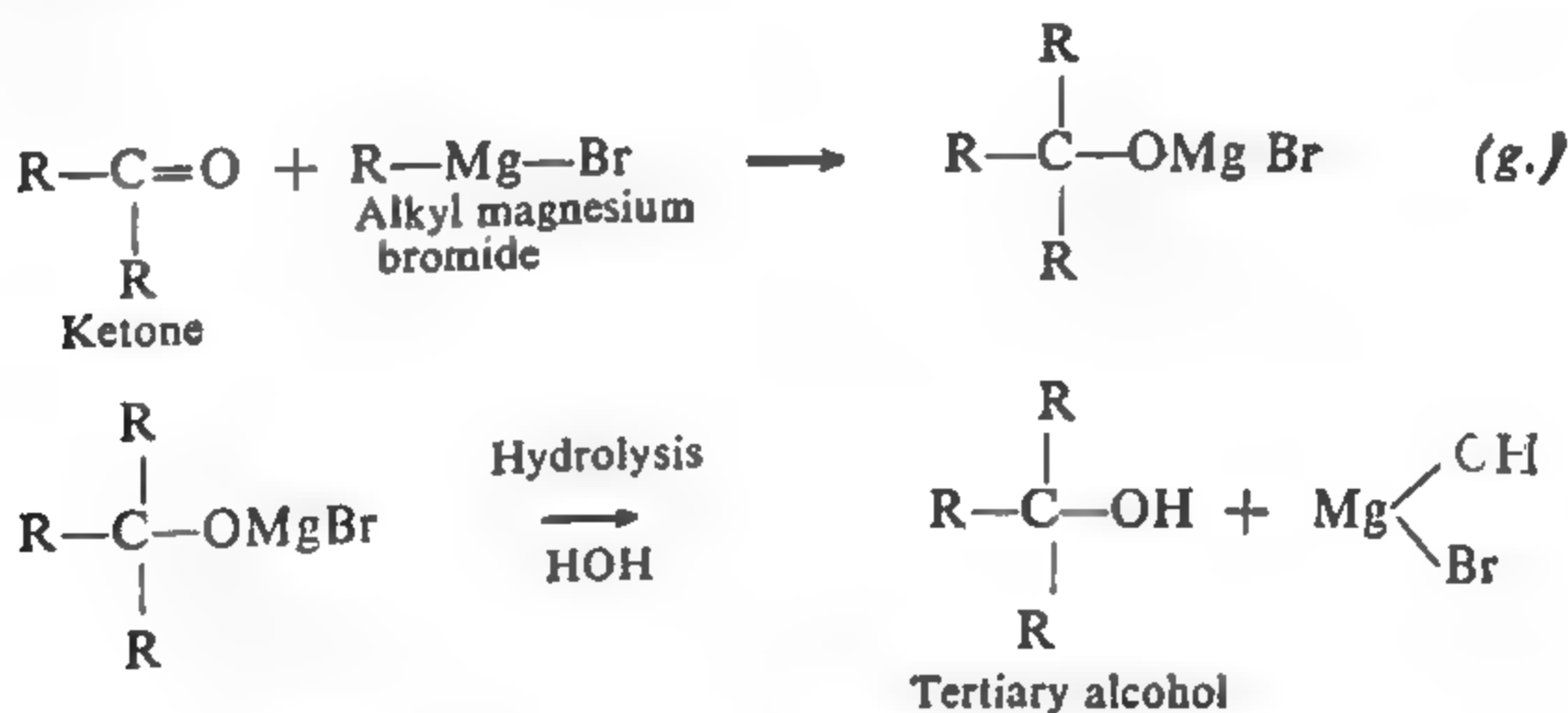
(i) *Primary alcohols* are obtained by the action of formaldehyde followed by hydrolysis.



(ii) *Secondary alcohols* are obtained by the action of aldehydes (except formaldehyde) followed by hydrolysis.



(iii) *Tertiary alcohols* are obtained by the action of ketones followed by hydrolysis.



(8) **By fermentation of carbohydrates.** Some alcohols can be prepared **industrially** by the fermentation of suitable carbohydrates with suitable ferments. For example, ethyl alcohol is obtained by the fermentation of cane-sugar or maltose sugar or glucose by yeast. (see Page 357)

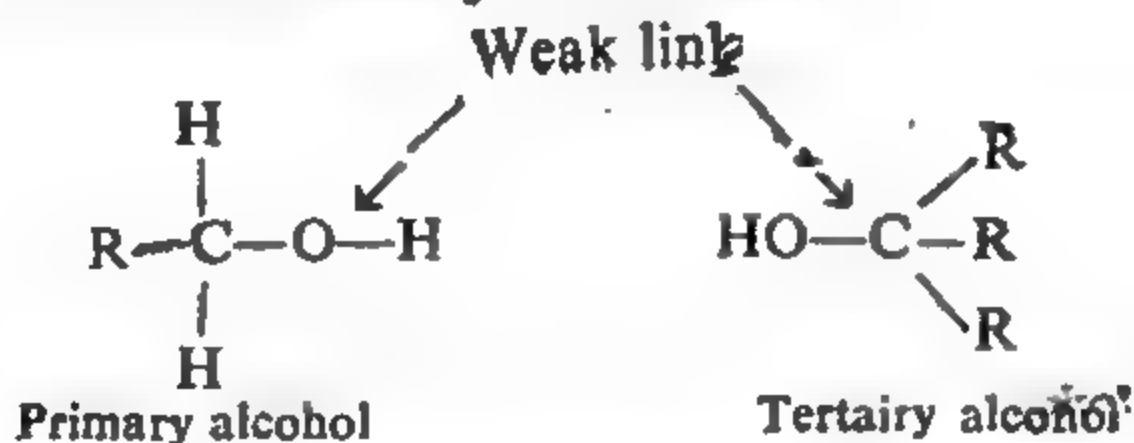
Physical Properties. The lower alcohols are colourless volatile liquids with a distinctive alcoholic smell and a burning taste. The higher members are solids and are almost odourless.

The first three members are completely miscible with water, the solubility decreases rapidly with rising molecular weights and the higher members are practically insoluble in water.

The boiling points and the specific gravities of alcohols increase regularly with the increasing molecular weight and in a group of isomeric alcohols, the primary alcohol has the highest boiling point and tertiary the lowest, while the secondary alcohol has an intermediate value.

Chemical Properties. The chemical properties of alcohols centre round the reactive hydroxyl (OH) group which is involved in reactions in two different ways. In one type of reactions, it is the H-atom of the OH group which takes part while in the other type of reactions, the (OH) group is involved as a whole.

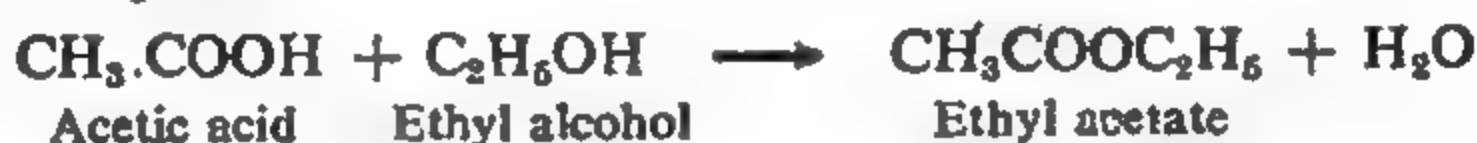
In the first type of reactions, the primary alcohols are the most reactive and the tertiary alcohols are the least while in the second type of reactions the order of reactivity is reversed.



(1) **Esterification.** Alcohols react with organic and inorganic acids to form esters.



For example,



The esters with halogen acids (inorganic acids) are the alkyl halides.



For example,



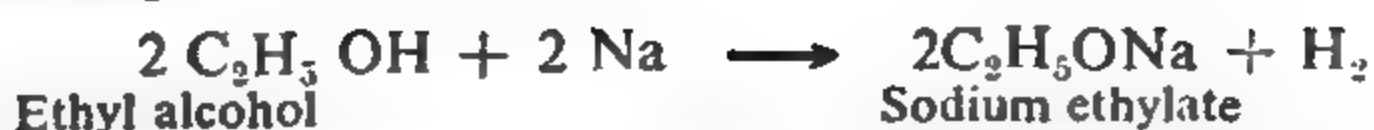
The order of reactivity of an alcohol with a given organic acid is primary > secondary > tertiary but with a given halogen acid, the order is reversed. This is due to the fact that the mechanism of esterification with organic acid is different from that with halogen acids. In case of the latter, it is the (OH) group which is replaced while with organic acids, it is the H-atom of the OH group which is involved, viz.,



(2) **Action of alkali metals.** Alcohols are readily attacked by strongly electropositive metals, such as sodium, potassium, forming *alcoholates* or *alkoxides* and liberating hydrogen.



For example,



(3) **Action of phosphorus halides.** When an alcohol is treated with phosphorus pentahalide, the hydroxyl group is replaced by halogen and an alkyl halide is formed.



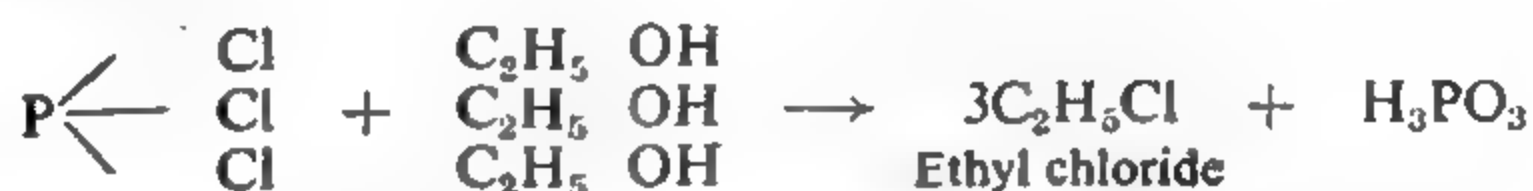
For example,



Since the reaction is accompanied by the evolution of HCl gas, it provides a ready test for the presence of (OH) group in an organic compound.

Alcohols also react with phosphorus trihalides to form alkyl halides.

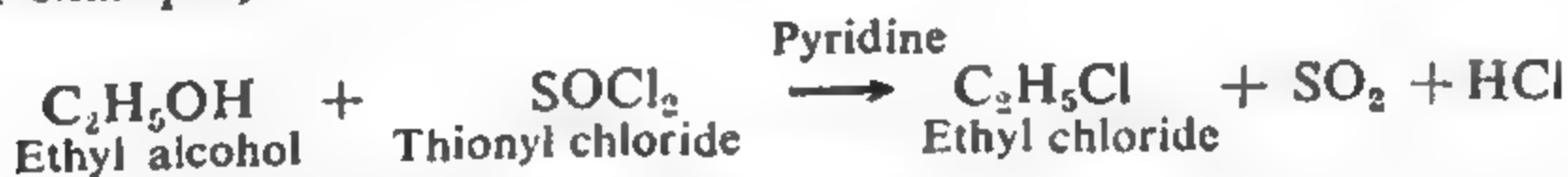
For example,



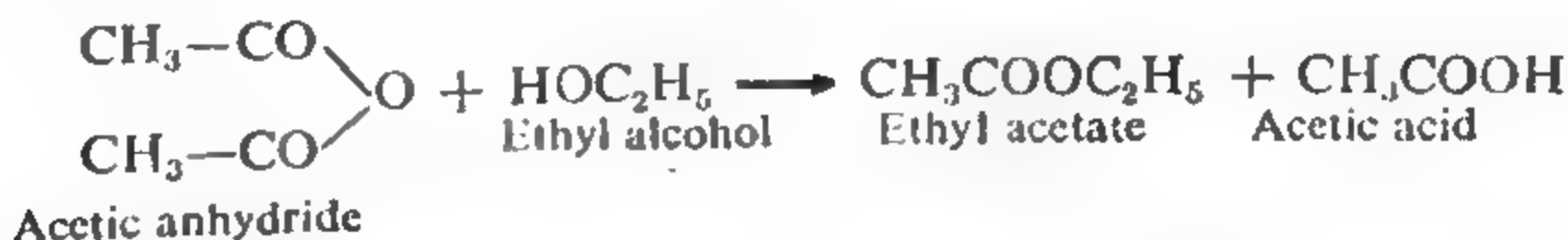
(4) **Action of thionyl chloride.** Alcohols also react with thionyl chloride in the presence of pyridine to form alkyl chlorides.



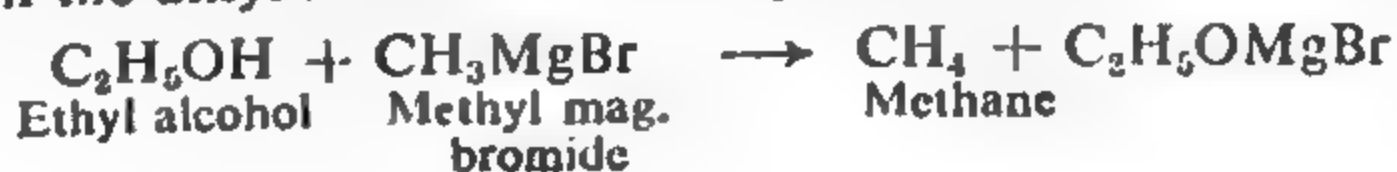
For example,



(5) **Action of acid halides and anhydrides.** These react with alcohols forming esters. For example,

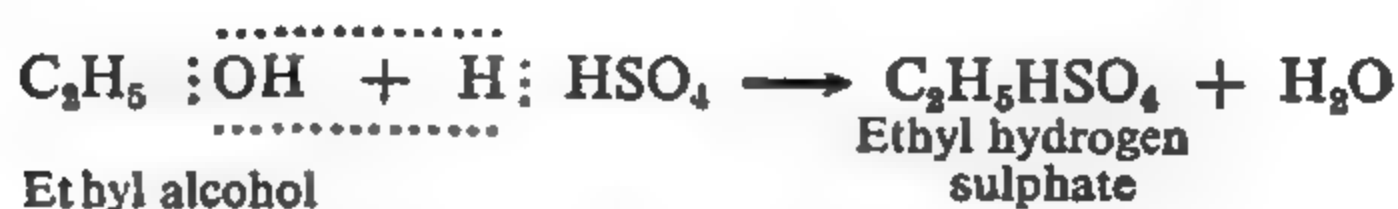


(1) **Reaction with Grignard reagents.** Alcohols react with Grignard reagents forming the corresponding paraffins. The H atom of OH group combines with the alkyl radical of the Grignard reagent. For example,



(7) **Action of concentrated sulphuric acid.** Action of sulphuric acid on alcohol is very interesting because it gives rise to a variety of products depending upon the conditions of the experiment.

The primary function of sulphuric acid, like other acids, is esterification, forming an alkyl hydrogen sulphate. For example,



This may give rise to three more products :

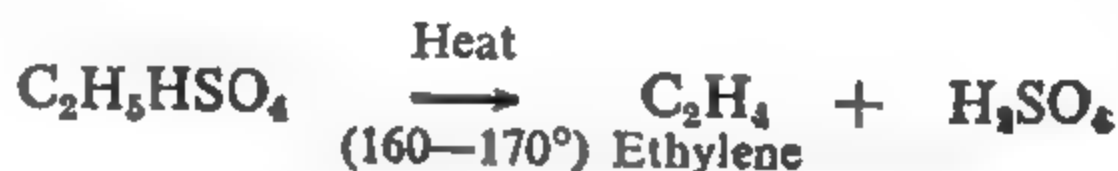
(i) When subjected to *vacuum distillation at low temperatures*, a dialkyl sulphate is formed.



(ii) When heated with *excess of alcohol*, ether is formed :

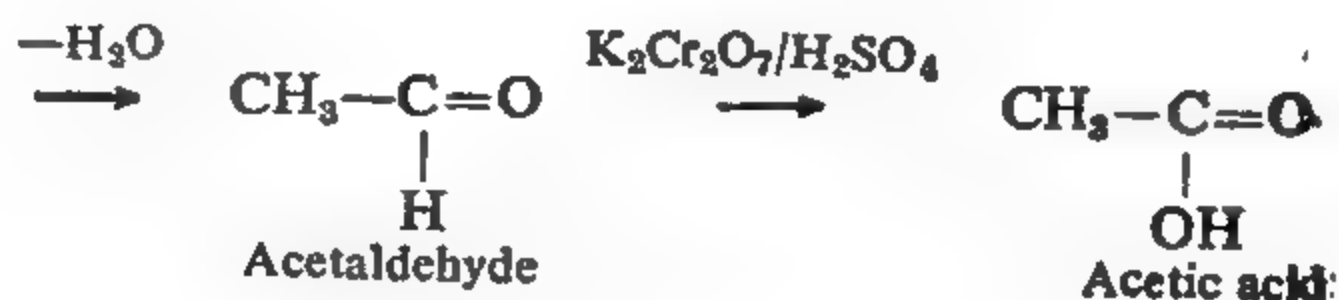
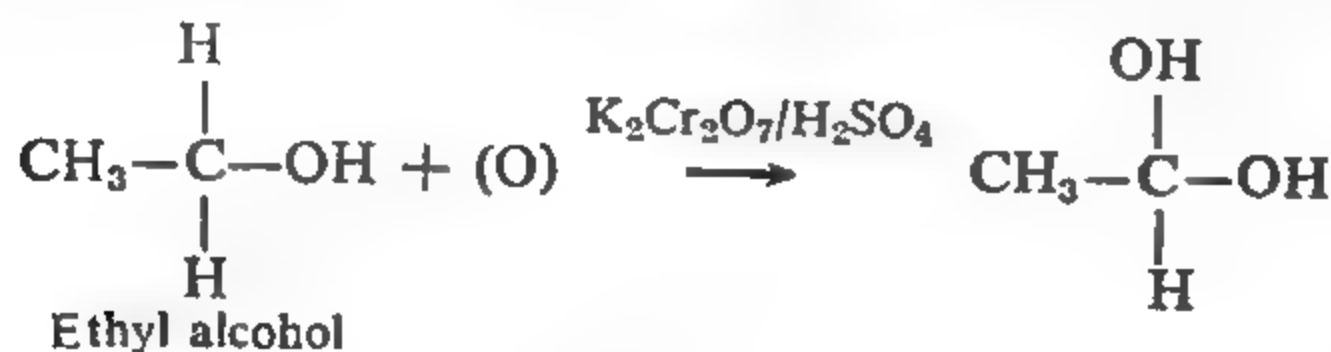


(iii) At higher temperatures in the presence of *excess of sulphuric acid* ethylene is produced.

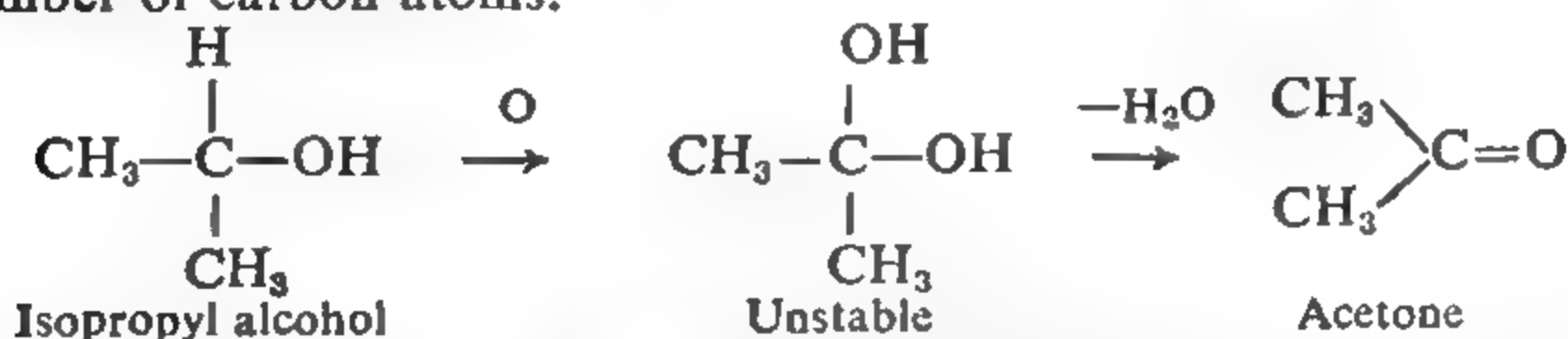


(8) **Oxidation.** Alcohols can be conveniently oxidised by alkaline or acidified KMnO_4 , acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or dil. HNO_3 and the products of oxidation depend upon the class of alcohols. Thus,

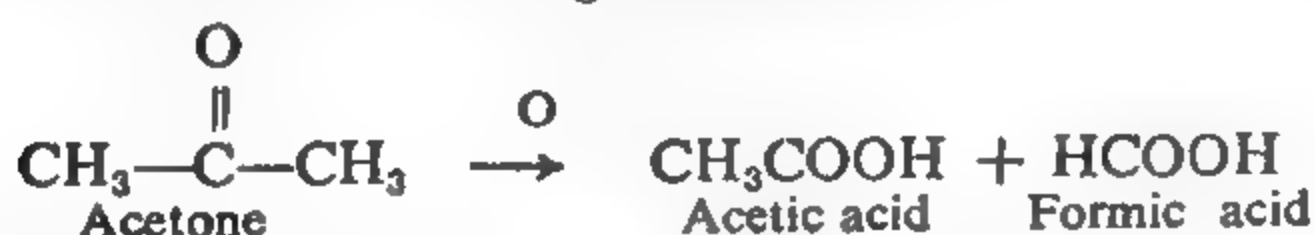
(i) A *primary alcohol* on oxidation gives first an aldehyde which on further oxidation yields an *acid*. Both the aldehyde and the acid contain the *same number of carbon atoms as the original alcohol*.



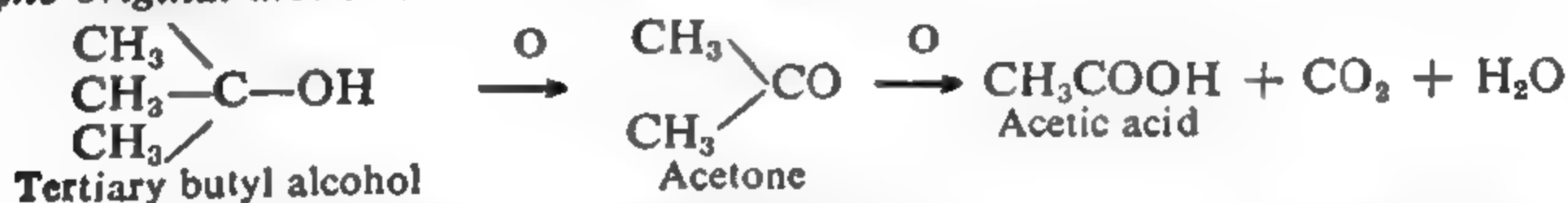
(ii) A secondary alcohol on oxidation gives a ketone with the same number of carbon atoms.



Ketones are not easily oxidised because they do not have any hydrogen with the "oxidised" carbon. On prolonged and drastic treatment, however, they break to give a mixture of acids with smaller number of carbon atoms than the original alcohol.

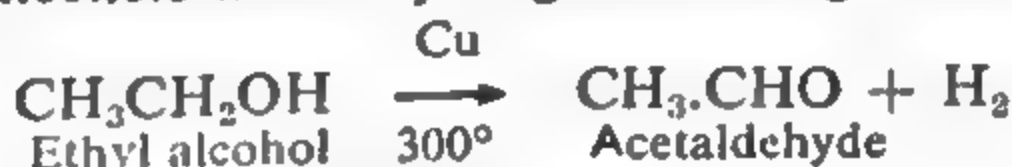


(iii) A tertiary alcohol is resistant towards oxidation in neutral or alkaline solution but is oxidised in acid medium to give a mixture of ketone and acid each containing smaller number of carbon atoms than the original alcohol.

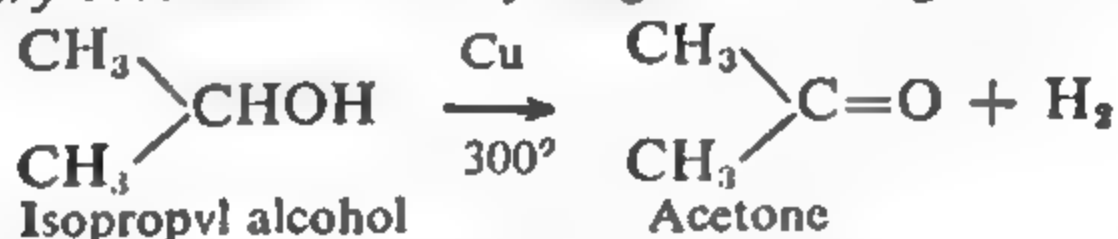


(9) Catalytic dehydrogenation. The three classes of alcohols behave differently when their vapours are passed over reduced copper at 300°.

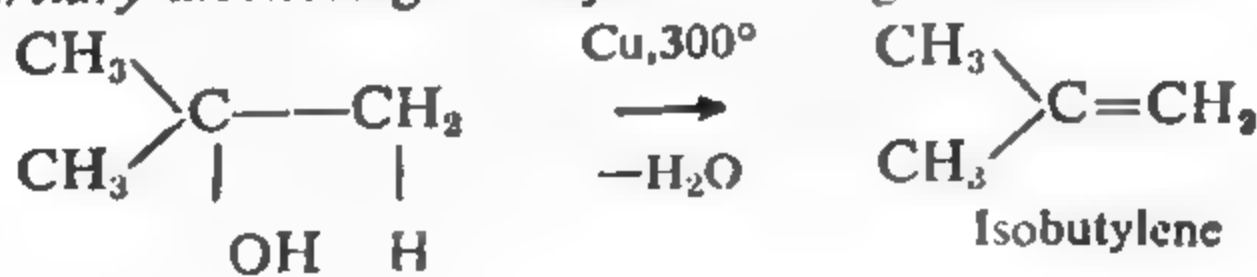
(i) Primary alcohols are dehydrogenated to give aldehydes.



(ii) Secondary alcohols are dehydrogenated to give ketones.



(iii) Tertiary alcohols get dehydrated to give olefins.



Detection of an OH Group.

The presence of hydroxyl group in an organic compound may be detected by the following tests :

- (i) Add a small piece of metallic sodium, hydrogen is evolved.
- (ii) Add a small amount of phosphorus pentachloride, hydrochloric acid gas is evolved.
- (iii) Add acetyl chloride or benzoyl chloride, HCl gas is evolved with the separation of an oily layer of the corresponding ester.
- (iv) Warm with anhydrous sodium acetate and concentrated sulphuric acid, a fruity smell of an ester is given out.

Methods of distinguishing between Primary, Secondary and Tertiary Alcohols.

(1) **Oxidation.** *Primary alcohols* on oxidation give first *aldehydes* and then acids. Both the aldehyde and the acid contain the same number of carbon atoms as the original alcohol.

Secondary alcohols on oxidation give *ketones* which on further drastic oxidation yield a mixture of acids, each acid containing fewer number of carbon atoms than the original alcohol.

Tertiary alcohols on oxidation with acid oxidising agents give a mixture of ketone and acid each containing fewer number of carbon atoms than the original alcohol. (see page 351).

(2) **Catalytic dehydrogenation** by passing over *reduced copper at 300°*.

Primary alcohols give *aldehydes*.

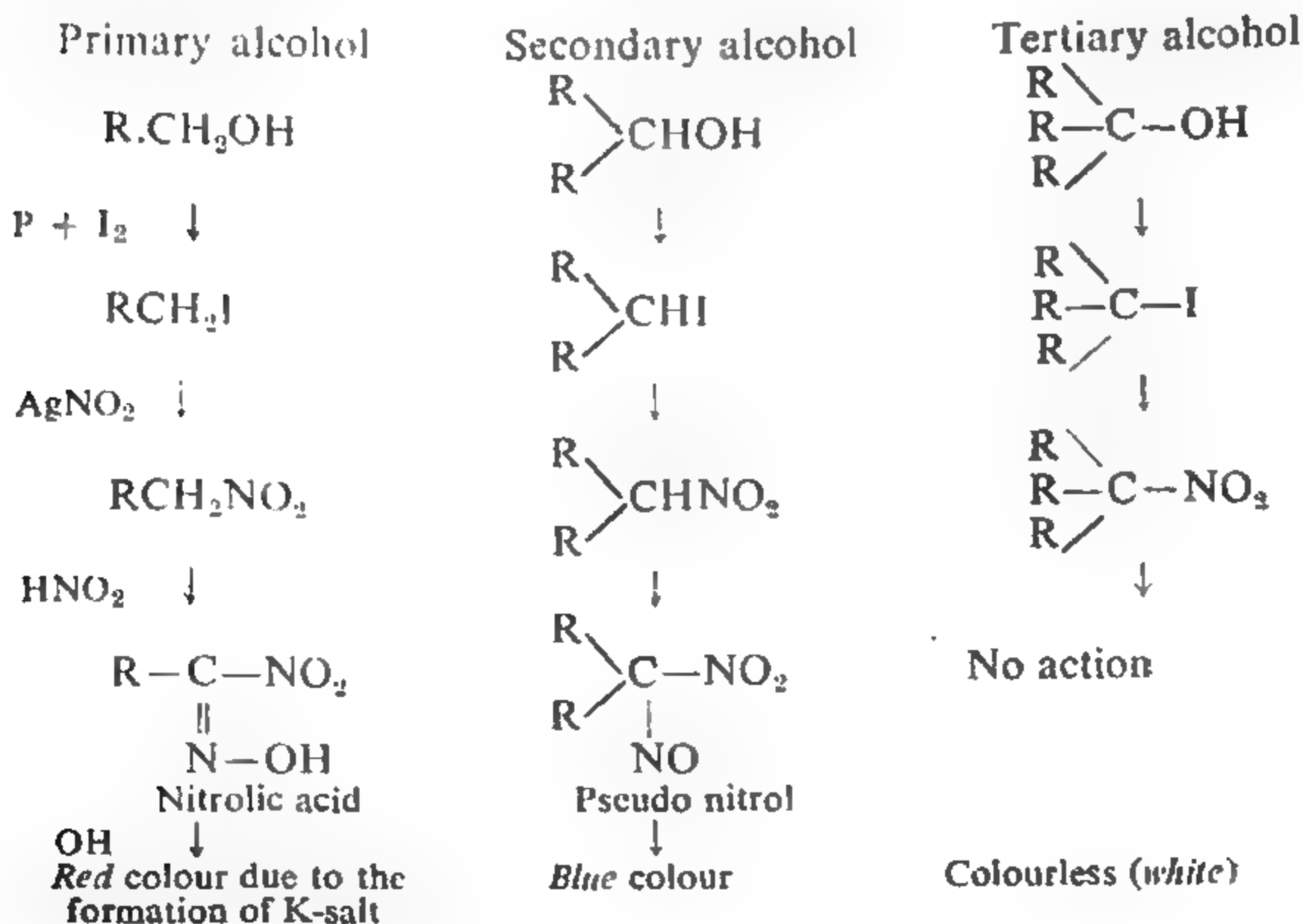
Secondary alcohols give *ketones*, and

Tertiary alcohols yield *olefins*. (see page 351)

(3) **Victor Meyer's Test.** "*Red, blue and white*" test.

The alcohol is converted by phosphorus tri-iodide into the corresponding iodide which is then heated with silver nitrite to yield the nitro-paraffin. The resulting nitro-paraffin is treated with nitrous acid and the alkalified. Characteristic colours are obtained depending upon the class of alcohol. Thus :

Primary alcohols produce *red* colour ; *secondary alcohols* produce *blue* colour while in case of the *tertiary alcohols*, the solution remains colourless (*white*).



INDIVIDUAL MEMBERS

METHYL ALCOHOL, METHANOL, CH_3OH

It occurs in nature in the form of methyl esters in the essential oils of certain plants. For example, oil of wintergreen contains methyl salicylate ; clove oil contains methyl benzoate and oil of jasmine and that of orange flowers contain methyl ester of anthranilic acid

Preparation. Methyl alcohol can be prepared by any of the general methods for the preparation of primary alcohols, described earlier.

Manufacture. The following three methods are available for the manufacture of methyl alcohol :

I. From Wood. The earliest method for the manufacture of methyl alcohol was from the destructive distillation of wood wherefrom the name "*wood spirit*" was derived for methanol.

Wood is cut into pieces of suitable size and placed in a wirework carriage which is rolled in a cast iron chamber (Fig. 1) and heated at temperatures between 250 and 400° for about 30 hours.

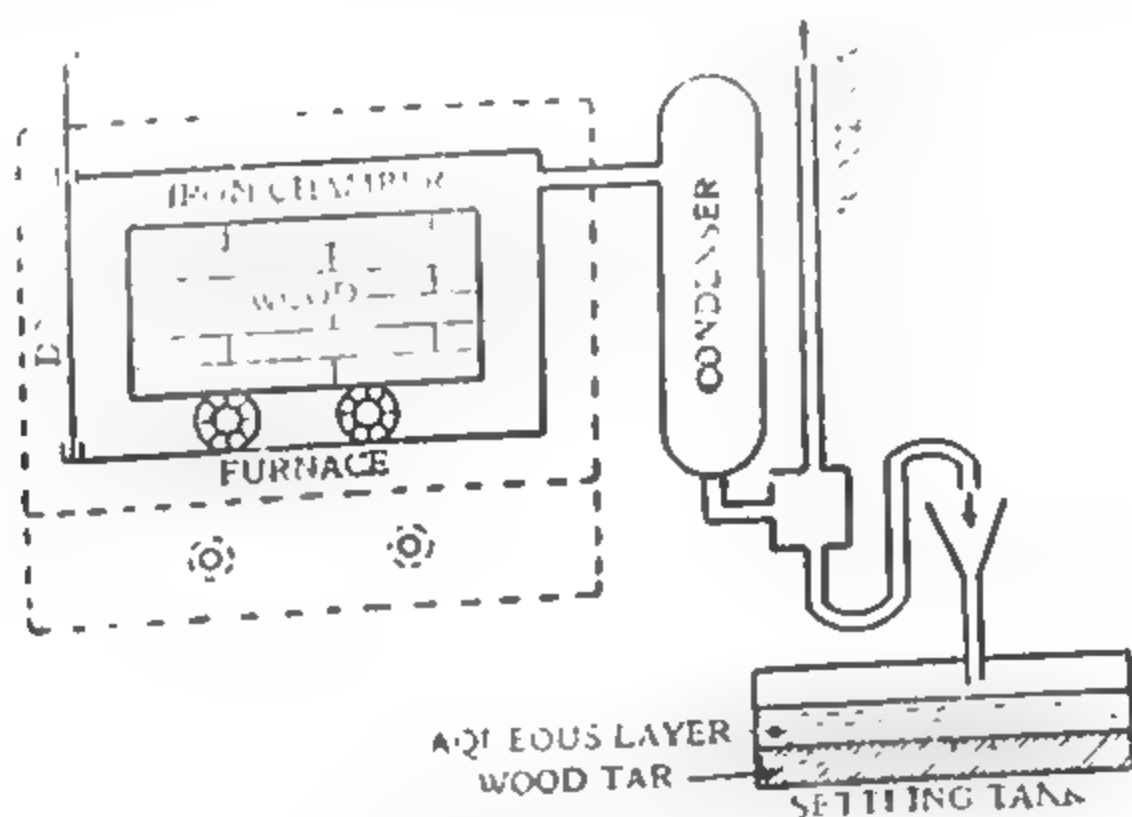


Fig. 1. Destructive Distillation of Wood.

The products of distillation are :

- (1) **Wood gas.** This is a gaseous mixture consisting of hydrogen, methane, carbon monoxide, carbon dioxide, oxygen and nitrogen. It is used as a fuel for heating the cast iron chambers mentioned above.
- (2) **Pyroligneous acid.** (*Pyro*, fire ; *lignum*, wood). This is an aqueous distillate containing about 10 per cent of acetic acid, 1-2 per cent methyl alcohol and 0.5 per cent of acetone.
- (3) **Wood tar.** It is a thick black liquid which separates from the aqueous distillate and contains compounds such as paraffins, naphthalene, phenols, etc.
- (4) **Wood charcoal.** It is left as a solid residue in the cast-iron chambers and is used as a domestic fuel.

Treatment of Pyroligneous Acid. The pyroligneous acid is treated as below for the recovery of acetic acid, acetone and methyl alcohol.

(i) **Recovery of acetic acid.** The pyroligneous acid is treated with lime and then distilled in a copper vessel when acetic acid is retained in the vessel as calcium acetate,



while methyl alcohol and acetone distil over along with water. The calcium acetate so obtained is distilled with dilute sulphuric acid to get a solution of acetic acid in water.



From this solution acetic acid is finally extracted by means of solvents like isopropyl ether.

(ii) **Recovery of methyl alcohol.** The distillate containing methyl alcohol and acetone, obtained in step (i) is dehydrated with quick lime and subjected to fractional distillation when *crude acetone* (b.p. 56°) and *crude methyl alcohol* (b.p. 65°) are obtained.

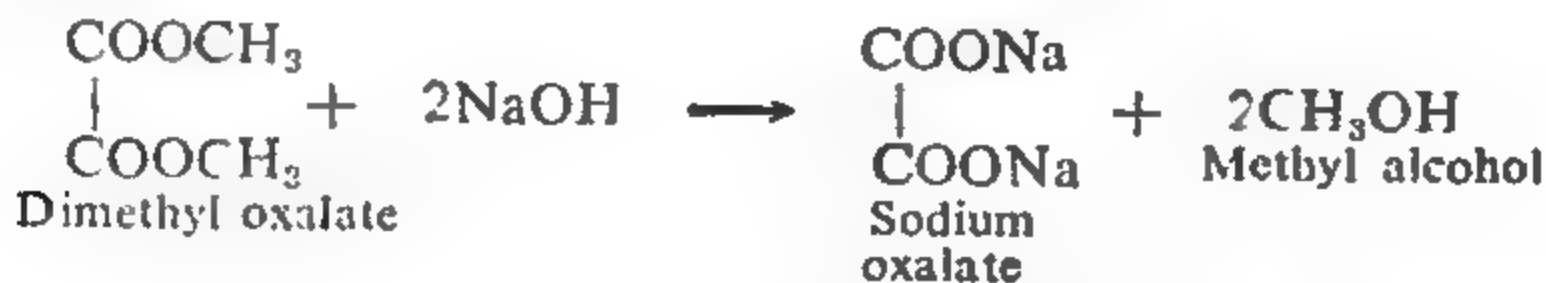
The *crude methyl alcohol* is diluted with water to throw out of solution any oily impurities which collect at the surface and are removed.

The aqueous layer is then treated with powdered anhydrous calcium chloride when methyl alcohol separates out in the form of a solid, crystalline compound of the composition $\text{CaCl}_2 \cdot 4\text{CH}_3\text{OH}$, leaving behind acetone and other impurities in the solution. The crystalline compound is separated and gently heated to drive off any acetone and then decomposed by distillation with water when methyl alcohol distils over. It is dehydrated by repeatedly distilling over quick lime.

Alternatively, the commercial alcohol may be heated with *anhydrous* oxalic acid, when on allowing the liquid to cool, crystals of dimethyl oxalate separate out.



These are subjected to suction on a filter pump, washed with a little water to free them from any contaminations and then hydrolysed by caustic soda.



The methyl alcohol thus set free is recovered by distillation and dehydrated by repeated distillation over quick lime and finally over metallic calcium.

This method is now becoming obsolete.

(iii) For recovery of pure acetone from crude acetone, see manufacture of acetone, chapter XXXIV.

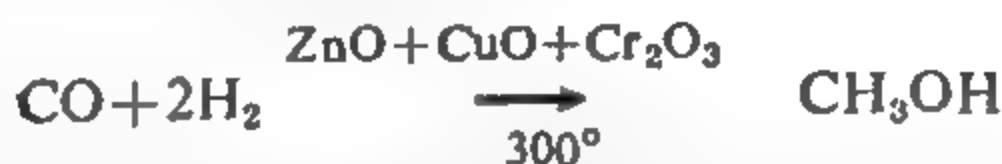
II. From Water Gas. At the present time, methyl alcohol is largely obtained synthetically by the hydrogenation of carbon monoxide.



For this purpose *water gas*, obtained by the action of steam on red hot coke,



is mixed with half its volume of hydrogen and passed at a *pressure of about 200 atmospheres* over a *catalyst* consisting of a mixture of oxides of copper, zinc and chromium, at 300°



By taking proper precautions almost cent per cent yield of methyl alcohol is obtained and the purity of the product is above 99 per cent.

A diagrammatic sketch of the plant used for the synthesis of methyl alcohol is shown in Fig. 2.

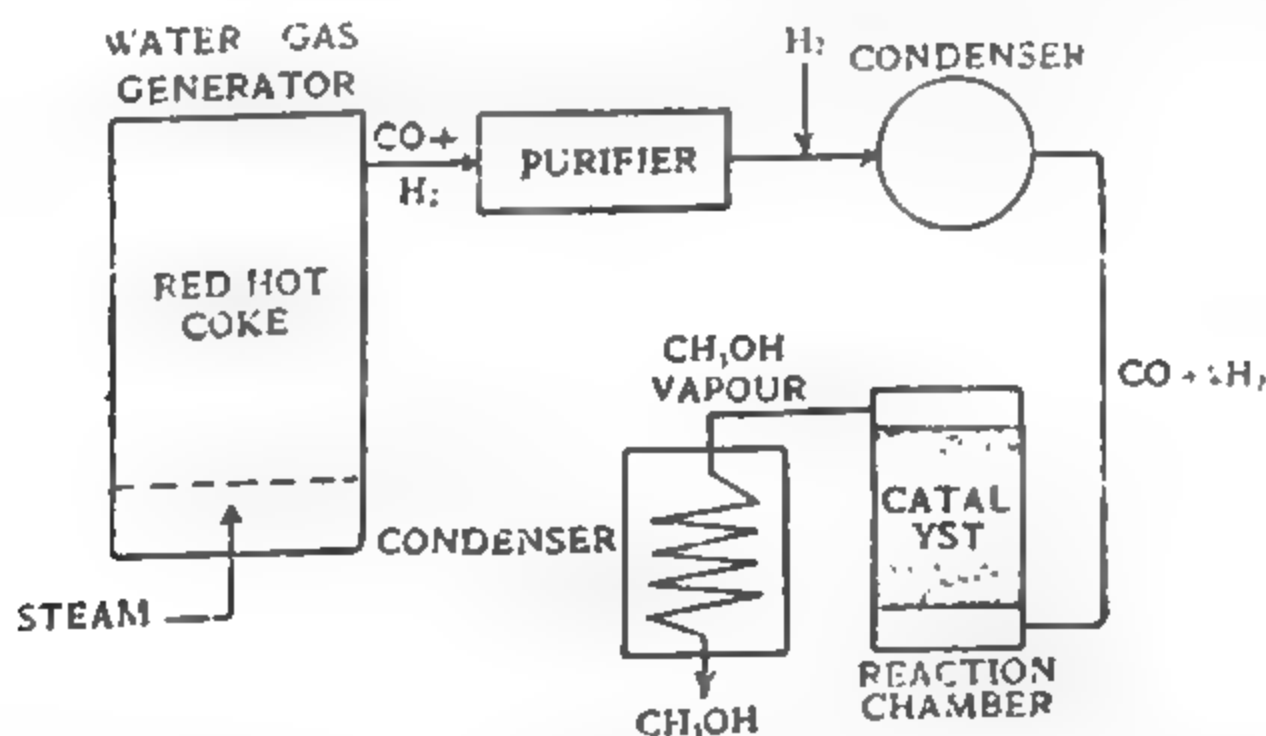
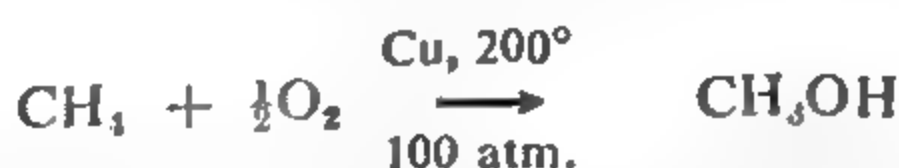


Fig. 2. Synthesis of methyl alcohol from water gas.

III. From Natural Gas. Methyl alcohol is also prepared on a commercial scale by the *catalytic oxidation* of methane obtained from natural gas. A mixture of methane and oxygen in the ratio of 9 : 1 by volume, is passed through a *copper tube* at 200° under a *pressure of 100 atmospheres*.



Properties. Methanol is a colourless liquid (b.p. 64.5°) with a characteristic, wine-like smell and a burning taste. It is poisonous, causing blindness, madness and even death depending upon the dose. In the body, it is slowly oxidised to formic acid which is highly toxic.

It is lighter than water (sp.g.=0.793) and is miscible with it in all proportions. It is a very good solvent for several organic substances.

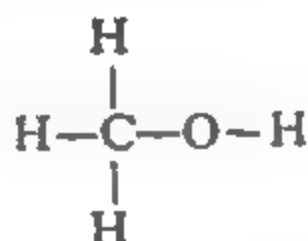
Chemically, it gives all the general reactions of alcohols.

Uses. Methyl alcohol is put to a number of commercial uses, important of which are given below :

(1) About one-third of the total production of methyl alcohol is used as an *antifreeze* for automobile and aeroplane radiators. (2) Another one-third is used as a *source of formaldehyde*. (3) Because of its highly poisonous nature, methanol is used for *denaturing* ethyl alcohol. (4) Methyl alcohol is an excellent *solvent* for oils, shellac, gum, etc., and is used in the *manufacture of varnish*. (5) Methanol is the only *single solvent* that can dissolve cellulose nitrate and hence it is largely employed in the manufacture of celluloid, guncotton, spray paints, and other nitro-cellulose products.

Structure. (1) The qualitative and quantitative analyses show that the molecular formula of methyl alcohol is CH_4O .

(2) Keeping in view the tetravalency of carbon, bivalency of oxygen and univalency of hydrogen, the only structural formula possible is



(3) Methyl alcohol reacts with sodium metal when only one of its hydrogens is replaced by sodium. This indicates that one hydrogen in methyl alcohol is in a different state of combination than the remaining three. This fact is well explained by the above structure.

(4) Methyl alcohol reacts with phosphorus pentachloride giving methyl chloride and hydrochloric acid gas. This again supports the above structure.



(5) The above structure is also confirmed by its synthesis from methyl chloride :



ETHYL ALCOHOL, ETHANOL, $\text{C}_2\text{H}_5\text{OH}$

This is the most important member of the series and is commonly named as "alcohol". It is usually produced in nature by the fermentation of carbohydrates and is thus present in plants to a very small extent in the free state and mostly in the form of its esters. It can also be detected in animal tissues and in the blood but only in traces.

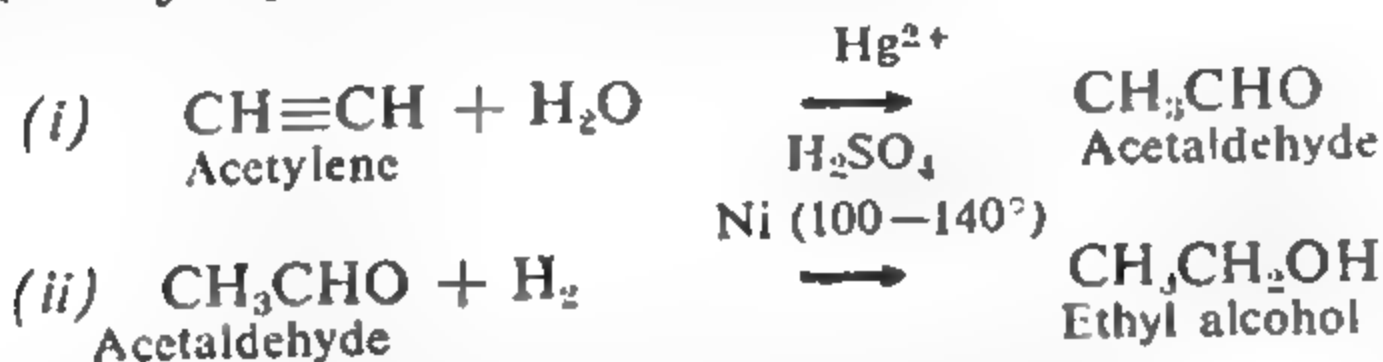
Preparation. Ethyl alcohol can be prepared by any of the general methods for the preparation of primary alcohols described earlier.

Manufacture. The most important methods for the manufacture of ethyl alcohol are :

- I. *Catalytic hydration of ethylene.*
- II. *Catalytic hydration of acetylene and subsequent reduction.*
- III. *Fermentation of sugars.*

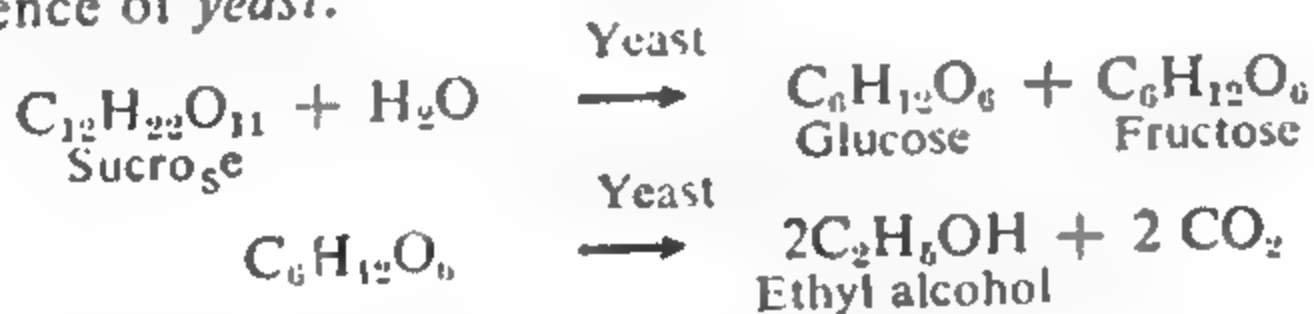
I. Alcohol from Ethylene. Large amounts of ethyl alcohol are obtained these days by the catalytic hydration of ethylene.

II. Alcohol from Acetylene. Acetylene when treated with dilute sulphuric acid in the presence of mercuric ions (catalyst) gives acetaldehyde which is further reduced by passing its vapour mixed with hydrogen over *finely divided nickel at 100–140°*.



III. Fermentation of Sugars. Fermentation is a process involving the slow decomposition of a complex organic compound into simpler ones through the agency of living organisms called *ferments*. As a matter of fact fermentation is brought about by the catalytic influence of complex non-living compounds, present in or produced by the ferments. These non-living compounds are called *enzymes* (= *in yeast*). For example, yeast contains three enzymes, *invertase*, *zymase* and *maltase* which bring about specific chemical reactions (see below) :

The term fermentation covers a variety of reactions such as conversion of sugars into alcohol (*alcoholic fermentation*), conversion of sugars into lactic acid (*lactic fermentation*), etc. Ethyl alcohol has been prepared since antiquity by fermentation of sugars, particularly glucose and sucrose in the presence of *yeast*.



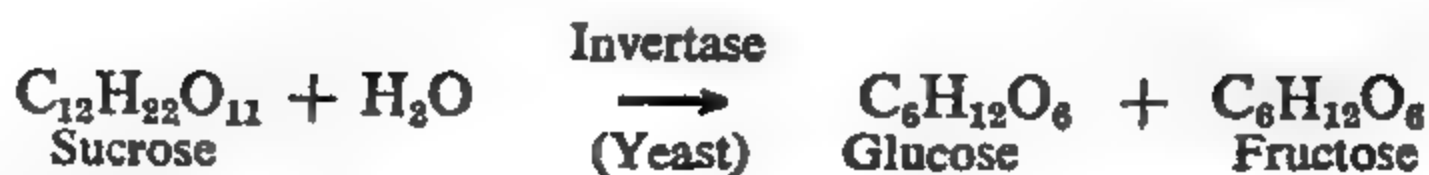
An economical source of sugar is *molasses*.

Alcohol from Molasses. Molasses—the mother liquor left after the crystallisation of cane-sugar from sugar-cane juice—still contains about 50 per cent by weight of sugar, mostly sucrose, glucose and fructose, and is used as an excellent cheap source for the production of ethyl alcohol.

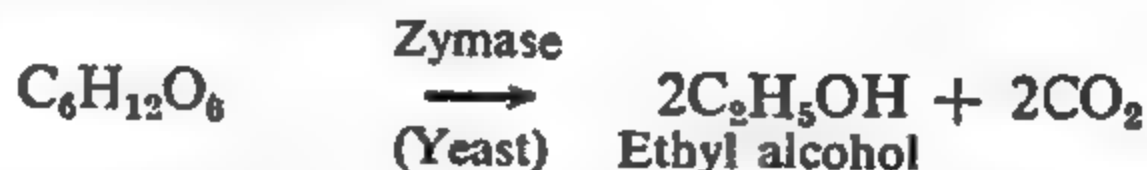
For this purpose, the molasses is diluted with water to reduce the concentration of sugar to about 10 per cent and slightly acidified with sulphuric acid : this will check the growth of any undesirable bacteria. Suitable quantities of ammonium sulphate and ammonium phosphate are added which will act as supplementary food for the yeast.

The liquid obtained above is placed in large fermentation tanks and maintained at temperature of about 35°. Yeast is now added ; fermentation starts accompanied by the following reactions :

(i) The enzyme *invertase*, present in yeast converts sucrose into glucose and fructose.



(ii) The enzyme *zymase* further converts the glucose and fructose into ethyl alcohol and carbon dioxide.

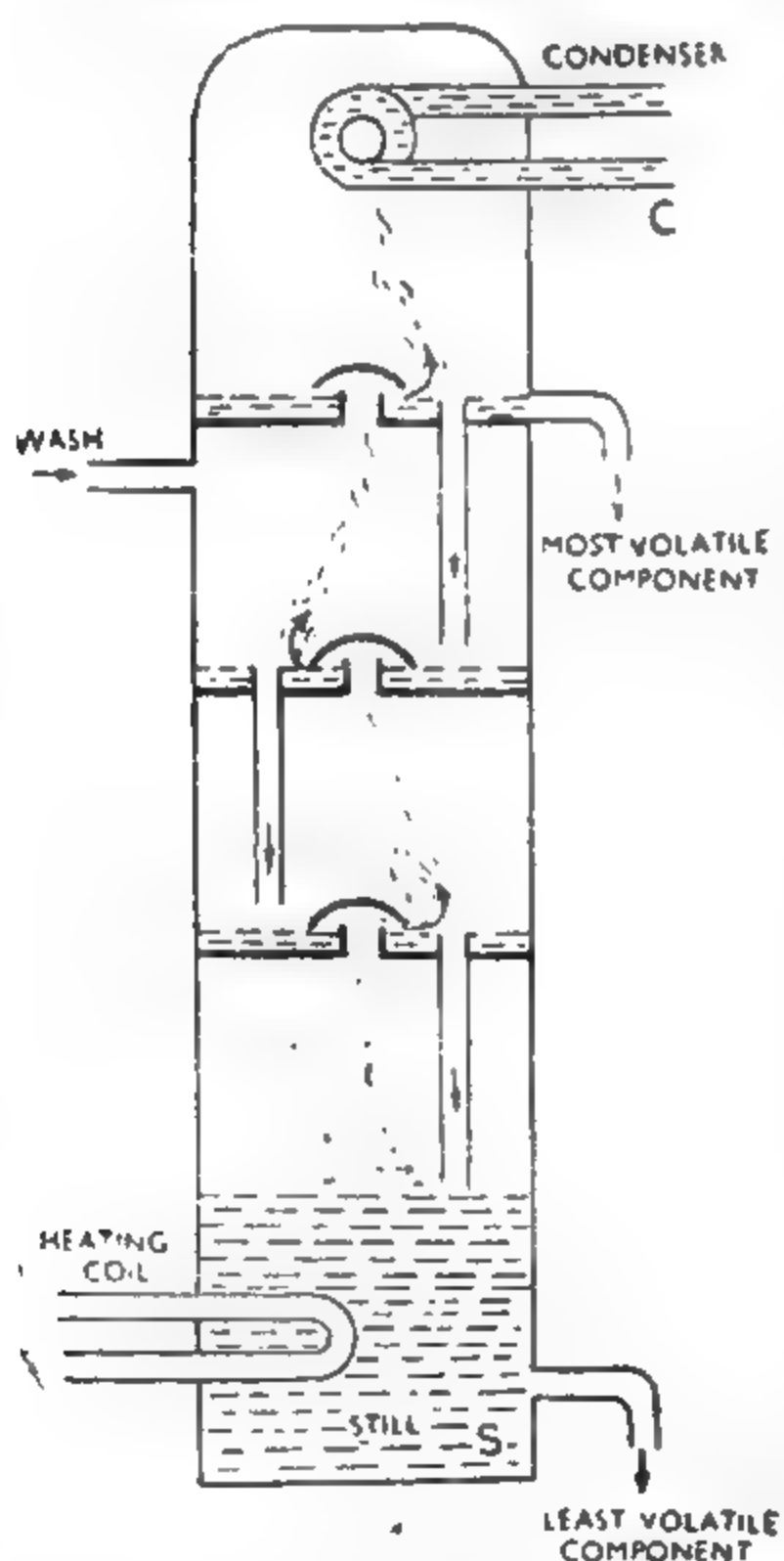


During fermentation, there is lot of frothing of the liquid due to the evolution of carbon dioxide *which is collected*. In order to keep the yeast alive and active, air is occasionally bubbled through the solution.

When the alcohol content of the fermented liquor rises to about 15–18 per cent, the yeast cells are killed and the process of fermentation stops automatically. This takes place in about 2–3 days time. The fermented liquid thus obtained is known as the '*wash*'. It is then subjected to fractional distillation.

A typical distillation plant is shown in Fig. 3.

It consists of three parts (i) A heated still *S* in which the mixture to be separated into its constituents is heated electrically (ii) The *fractionating column* proper which consists of a series of plates with small perforations and (iii) A condenser *C*, at the top.



The fermented liquor (*wash*) is admitted into one of the plates through the side tube as shown. This overflows to the plate below through the small openings. As the wash in the still is heated, the vapours as they rise are forced to bubble through the liquid on the plates. On doing so, they are cooled and get partially condensed, the less volatile constituent condensing to a greater extent. The vapours which rise from each plate upward are, therefore, much richer in the more volatile component, while the liquid which trickles down to the plate below is richer in the less volatile component. This process takes place at each plate. Thus ultimately the most volatile component escapes from the uppermost plate and the least volatile component returns to the still.

Fig. 3. A plate column.

(1) *First runnings*. This is a more volatile fraction consisting mainly of acetaldehyde and is used as an important source of acetaldehyde.

(2) *Rectified spirit or Industrial alcohol*. This consists of 93–95 percent (by weight) of ethyl alcohol.

(3) *Final runnings or fusel oil*. This is obtained between the range 125–140° and is a mixture of propyl, butyl, amyl alcohols. The main constituent, however, is iso-amyl alcohol. Fusel oil is used for the preparation of amyl acetate, which is employed as a solvent for varnishes and also in confectionery.

(4) The residual liquid left in the distillation plant is known as *spent-wash*. Because of its high nitrogenous content, spent wash is used as a cattle fodder.

Alcohol from Starch. Large amounts of alcohol are prepared from starch and other polysaccharides. Since *yeast* cannot bring about the fermentation of polysaccharides, the latter are first converted into sugars, by an enzyme, *diastase*. The important starchy materials are : potatoes, maize, barley, rice, etc.

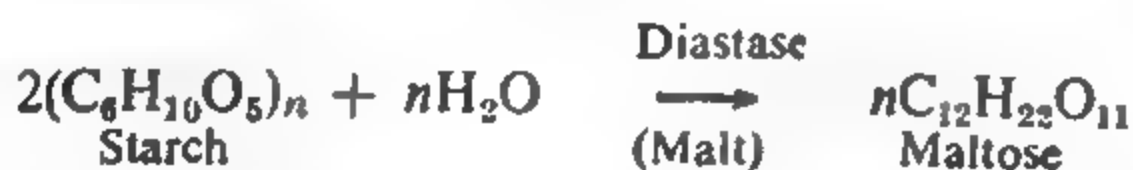
The various steps involved in the production of alcohol from a starchy material are :

- (i) *Malting*, that is, preparation of malt.
- (ii) Liberation of starch from the starchy material.
- (iii) *Saccharification*, that is, conversion of starch into maltose sugar.
- (iv) *Fermentation*, that is, conversion of maltose sugar into alcohol.
- (v) *Rectification*, that is, fractional distillation of fermented liquor.

(i) **Malting. (Preparation of Malt)** Barley is moistened with water and spread in a room in layers about 5 inches thick and allowed to germinate in the dark at about 15°. After a suitable length of time, the germination is stopped by heating the barley to about 60°. The germinated product is technically known as *maltase*. This is a rich source of the enzyme, *diastase*.

(ii) **Liberation of starch.** The starchy material (potatoes, rice, maize or barley) is rasped or crushed and then treated with steam at 140–150° under pressure when the starch present in the material is brought into solution. This solution is called the *mash*.

(iii) **Saccharification.** Malt obtained in (i) is added to the mash, kept at 50°. The enzyme *diastase* present in malt converts the starch into maltose sugar.



The process is complete in about one hour.

Alternatively, the starch may be converted into glucose by heating with dilute sulphuric acid or hydrochloric acid.



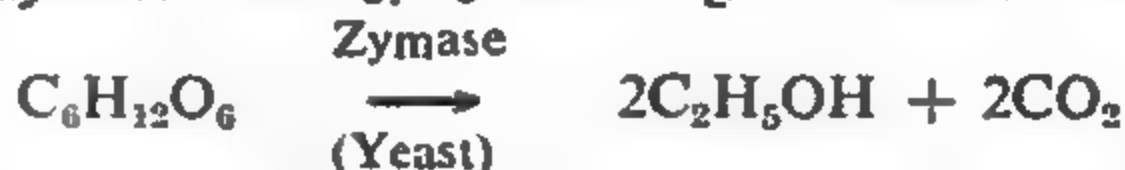
The excess of the acid is neutralised by adding lime.

(iv) **Fermentation.** The maltose (glucose) solution obtained above is cooled to about 30° and fermented by yeast when the following reactions take place :

(a) The enzyme *maltase* present in yeast converts maltose sugar into glucose.



(b) The enzyme *zymase* further converts glucose into alcohol and carbon dioxide.



Obviously, if the starch has been hydrolysed by dilute mineral acids, the glucose present in the resulting solution is directly attacked by *zymase* to give alcohol, *maltase* playing no part.

The fermented liquor contains about 10 per cent alcohol and is subjected to fractional distillation to obtain industrial alcohol (95% alcohol)

Absolute alcohol. Since ethyl alcohol forms a constant boiling mixture with water containing 95.57% by weight of the alcohol which boils at 78.15° , a temperature slightly lower than the boiling point of absolute alcohol, viz., 78.3° , it is not possible to effect a complete separation of ethyl alcohol from water by fractional distillation. Absolute alcohol containing only 0.3% water, can be prepared by chemical methods, for example, by distilling repeatedly over fresh quick lime which combines with water but not with alcohol. The last traces of water can be removed by distilling over a requisite amount of metallic sodium or magnesium or calcium.

On a large scale, absolute alcohol is prepared by the *azeotropic* distillation of industrial alcohol.

For this purpose, a suitable amount of benzene is added when a *ternary azeotropic mixture* of composition 18.5% alcohol, 7.4% water and 74.1% benzene, boiling at 64.85° (at atmospheric pressure) is obtained. Thus almost the entire amount of water present in industrial alcohol goes to form the ternary azeotropic mixture which passes over while almost 100% ethyl alcohol remains behind as residue.

Power alcohol. Power alcohol is a mixture of petrol and absolute alcohol or of industrial alcohol, petrol, and benzene. This mixture is used for generating power, especially in those countries in which the petroleum resources are meagre.

Denatured alcohol or Methylated spirit. The industrial alcohol is mixed with poisonous substances such as methyl alcohol, acetone or pyridine to render it unfit for drinking purposes. The product is put in the market under the name '*methylated spirit*' or '*denatured alcohol*' and is extensively used for making varnishes. It is also used as a disinfectant.

Properties. Ethyl alcohol is a colourless inflammable liquid, boiling at 78.3° . It has a typical alcoholic odour and a burning taste. It is miscible with water in all proportions and is also miscible with most of the organic solvents. It is a good solvent for oils, fats, resins, etc. It also dissolves inorganic substances such as caustic soda, caustic potash, phosphorus, sulphur, etc. Unlike methyl alcohol it is not poisonous. It rather acts as a good stimulant if taken in small doses.

Chemically it gives all the general reactions of alcohols.

Ethyl alcohol and methyl alcohol, resemble each other very closely but they can be distinguished from each other by the following reactions:

(i) Ethyl alcohol gives iodoform with iodine and sodium hydroxide while methyl alcohol does not.

(ii) Ethyl alcohol on oxidation gives acetic acid whereas methyl alcohol gives formic acid. (These two acids can be easily distinguished).

Uses. Ethyl alcohol is used :

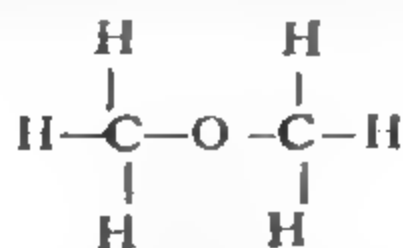
(1) For the preparation of esters, ether, chloral, etc. (2) As a solvent for gums, resins, paints, varnishes, etc. (3) As a fuel for lamps and stoves. For convenience of transportation, it is converted into **solid alcohol** by dispersing it in saturated calcium acetate containing a little stearic acid. (4) As a preservative for biological specimens. (5) As a low freezing and mobile liquid in scientific apparatus like thermometers, spirit level, etc. (6) Power alcohol is mixed in petrol in the ratio of 20 per cent and is used as a motor fuel.

Tests. 1. Ethyl alcohol when warmed with anhydrous sodium acetate and concentrated sulphuric acid gives a fruity smell due to the formation of ethyl acetate.

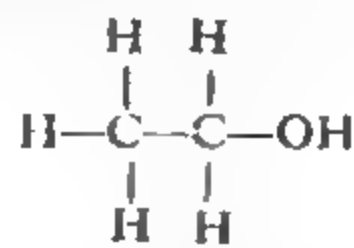
2. Ethyl alcohol, when warmed with iodine and sodium hydroxide, gives iodoform which has a characteristic smell.

Structure (1) The analytical data show that the molecular formula of ethyl alcohol is C_2H_6O .

(2) Assuming that carbon is tetravalent, oxygen bivalent and hydrogen monovalent, two structures, are possible for ethyl alcohol.



(I)



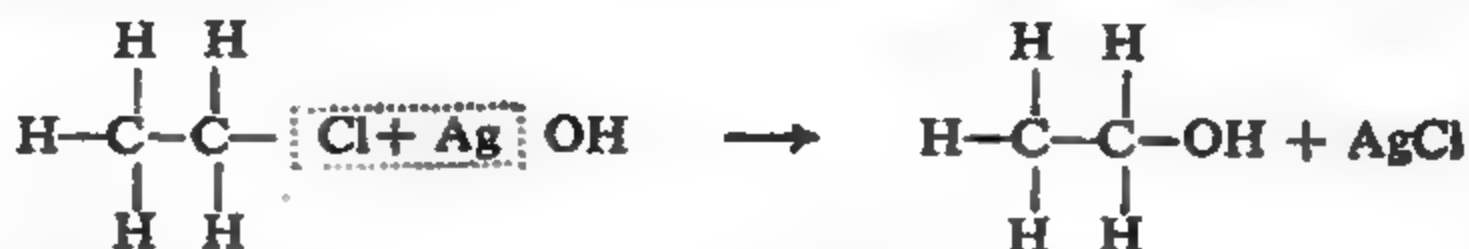
(II)

(3) Ethyl alcohol reacts with sodium metal when only one of its hydrogens is replaced by sodium. This indicates that one hydrogen atom in alcohol is in a different state of combination than the remaining five. In structure (I) all the six hydrogen atoms are equivalent but in (II), one hydrogen attached to oxygen is obviously different from the remaining five.

(4) Ethyl alcohol reacts with phosphorus pentachloride giving ethyl chloride and liberating hydrochloric acid gas. This indicates the presence of a hydroxyl group in its molecule.

It follows from (3) and (4) that ethyl alcohol has structure (II) and not (I).

(5) The above structure of ethyl alcohol is further supported by its synthesis from ethyl chloride.

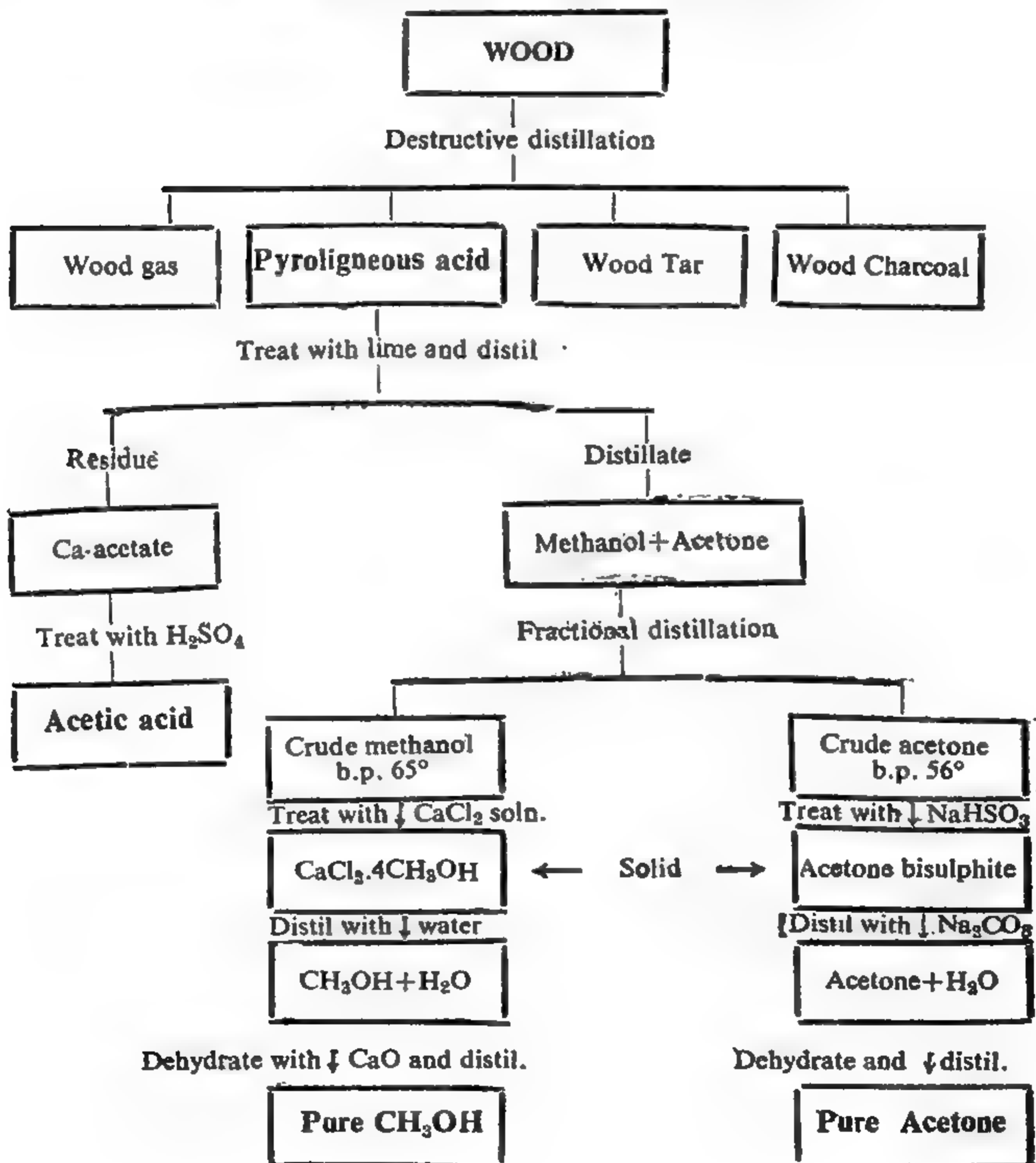


Formula (I) has been shown to represent another compound, dimethyl ether, which has very little resemblance to ethyl alcohol, physically or chemically.

Thus formula (II) is accepted as the structure of ethyl alcohol. It explains all the known properties of ethyl alcohol.

SUMMARIES

PRODUCTS FROM WOOD DISTILLATION



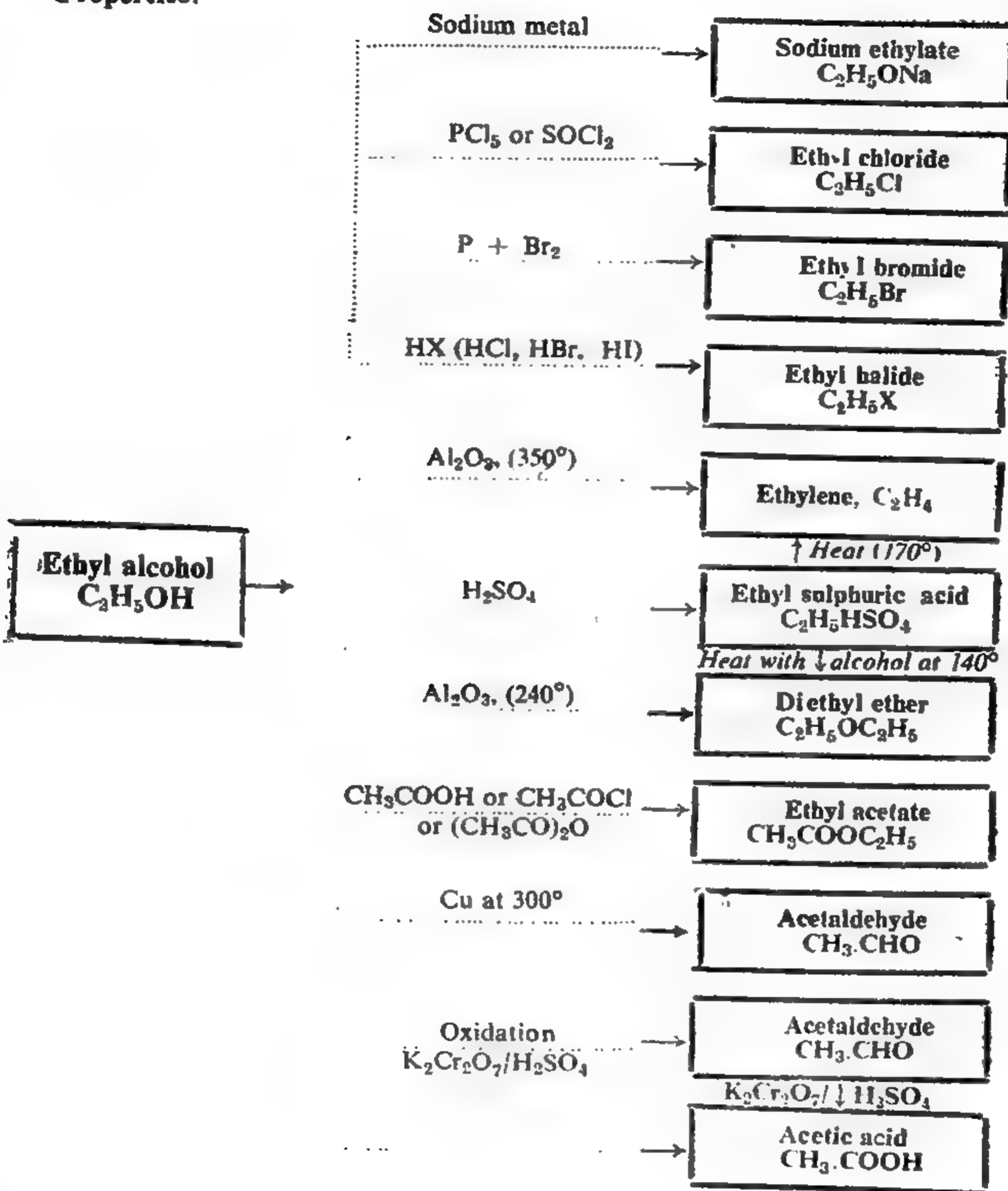
PREPARATION AND PROPERTIES OF ETHYL ALCOHOL

Preparation.

Ethyl bromide C_2H_5Br	Hydrolyse with KOH aqueous or AgOH →	
Ethylene C_2H_4	Catalytic hydration Al_2O_3 low temp, high pressure →	
Ethyl sulphuric acid $C_2H_5HSO_4$	Boil with water →	
Ethyl ether $C_2H_5OC_2H_5$	Hydrolysis with H_2SO_4 →	
Ethyl acetate $CH_3COOC_2H_5$	Hydrolyse with acid or alkali →	
Ethyl amine $C_2H_5NH_2$	Treat with nitrous acid ($NaNO_2/HCl$) →	→ Ethyl alcohol C_2H_5OH
Acetaldehyde CH_3CHO	Reduction with nascent hydrogen →	
Grignard reagent CH_3MgBr	Treat with $H.CHO$ and hydrolyse →	
Sugars Diastase ↑ Malt	Fermentation by yeast →	
Starch		
Acetic acid CH_3COOH	Reduction with $LiAlH_4$ →	
$CH_3COOC_2H_5$ or CH_3COCl or $(CH_3CO)_2O$	Reduction with $LiAlH_4$ →	

3995 -
2995

Properties.



QUESTIONS

1. What are alcohols? How are they classified?
2. Describe the general methods for the preparation of monohydric alcohols. Which of these methods can be successfully employed for the manufacture of ethyl alcohol?
3. What are Primary, Secondary and Tertiary alcohols? How would you distinguish between them?
4. How is methanol obtained from wood distillation? Describe its important properties and uses.

5. Describe in detail the manufacture of ethyl alcohol by methods other than fermentation. Give its typical reactions and uses.

6. Starting from a carbohydrate, how would you obtain rectified spirit, methylated spirit, absolute alcohol and power alcohol?

7. Describe the preparation and properties of ethyl alcohol. How is it distinguished from methyl alcohol?

8. What are monohydric alcohols? Give their characteristic reactions.

9. Describe the manufacture of ethyl alcohol from molasses. How has its structure been established?

10. Mention the different types of materials that may be utilised for the manufacture of ethyl alcohol and describe how the conversion is effected? How may it be prepared, starting from inorganic materials?

11. Describe in details the manufacture of methanol by the destructive distillation of wood. (Panjab Inter 1961)

12. Describe the manufacture of ethanol from molasses or starch. (Panjab Inter 1960 S)

13. State the reactions and the experimental conditions to obtain a Primary Alcohol from the following type of compounds:

- (i) An alkyl hydrogen sulphate (ii) An ester (iii) A Grignard's reagent (Panjab Inter 1959)
(iv) An amine

14. Illustrate by chemical equations the variation of chemical properties of an alcohol with the position of alcoholic group in a carbon chain. (Panjab Inter 1957S)

15. What do you understand by 'destructive distillation of wood'? Give the names and rough composition of the products thus obtained.

Describe the manufacture, by this method, of any one of the organic compounds that you have studied. Give the important reactions of the compound described. (Panjab Inter 1954)

16. State and represent eight important chemical properties of aliphatic monohydric alcohols. (Panjab Inter 1956)

17. Explain how the following are obtained from potatoes:

- (i) Rectified spirit. (ii) Methylated spirit. (iii) Absolute Alcohol. (Panjab Inter 1951)

What are the important uses of ethyl alcohol?

18. How would you differentiate the isomers: $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CHOHCH}_3$? (Panjab Inter 1950)

19. Fill in the blanks:

- (i) Primary, secondary and tertiary alcohols are characterised by the presence of....,....and....groups respectively.
(ii) An.....on hydrolysis yields an alcohol and an acid.
(iii) The two sources for the industrial manufacture of ethanol are.....and.....
(iv) A primary alcohol yields on.....an aldehyde and on further oxidation... containing the same of carbon atoms as are present in the original alcohol.
(v) A tertiary alcohol gives an.....on being passed over hot reduced copper whereas a primary and a secondary alcohol giveand.....
(vi) Pyroligneous acid is one of the products of.....of wood and it is one of the chief sources for the manufacture of.....and.....
(vii) A primary alcohol can be got when a primary.....is treated with nitrous acid.

20. Describe the manufacture of methyl alcohol from wood distillation and from water gas. Give its tests and uses. (Panjab T.D.C. Part I 1963 S)

21. How is ethyl alcohol manufactured from molasses? Explain the terms rectified spirit, methylated spirit and absolute alcohol. Give uses of alcohol. (Panjab T.D.C. Part I 1964)

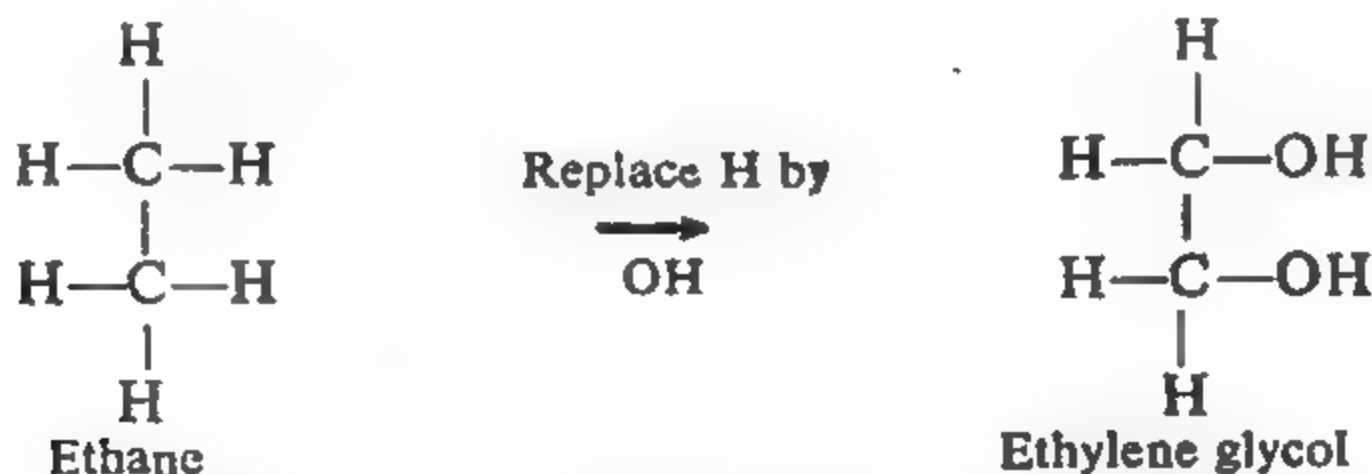
CHAPTER XXXII

POLYHYDRIC ALCOHOLS

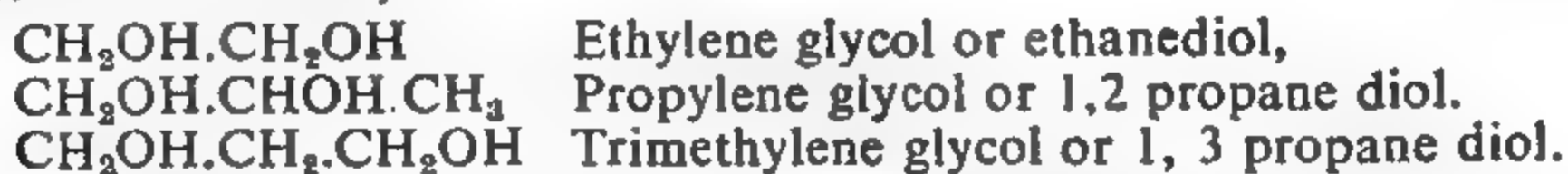
DIHYDRIC ALCOHOLS—GLYCOLS

As mentioned in the previous chapter, *dihydric alcohols* are compounds containing two hydroxyl groups. Because of their sweet taste they are called *glycols* (Greek, *glyk*—meaning sweet). The two hydroxyl groups must be attached to two different carbon atoms because, as a rule, the compounds containing more than one hydroxyl groups attached to the same carbon atom are unstable and immediately lose a molecule of water.

Glycols may be considered to be derived from alkanes by replacing two hydrogen atoms attached to *different* carbon atoms by hydroxyl groups.



The names of glycols are derived from the alkenes or the polymethylenes from which they are formed. Their I.U.C. name is *alkane-diols*. For instance,



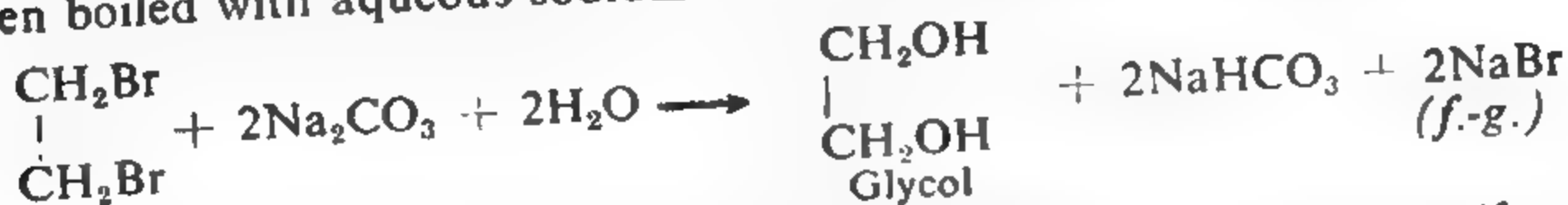
Ethylene Glycol, (1, 2-ETHANE DIOL) CH₂OH.CH₂OH

Preparation. Ethylene glycol may be prepared by the following methods :

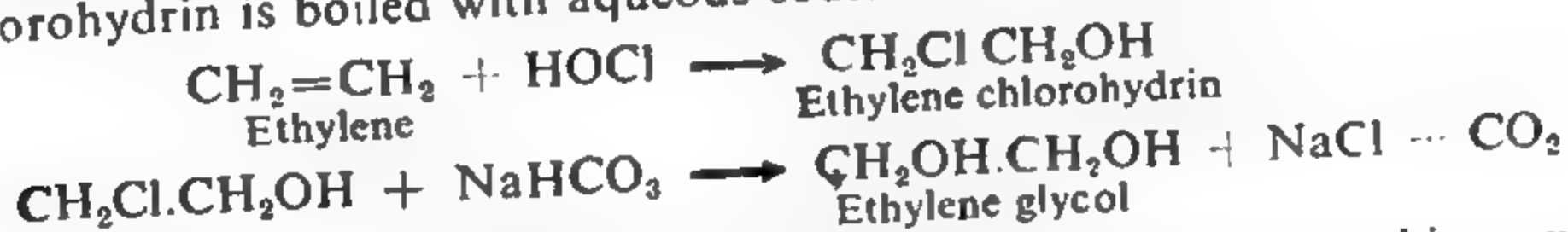
(i) **By the oxidation of ethylene.** Ethylene when passed into a dilute cold, alkaline solution of potassium permanganate yields glycol.



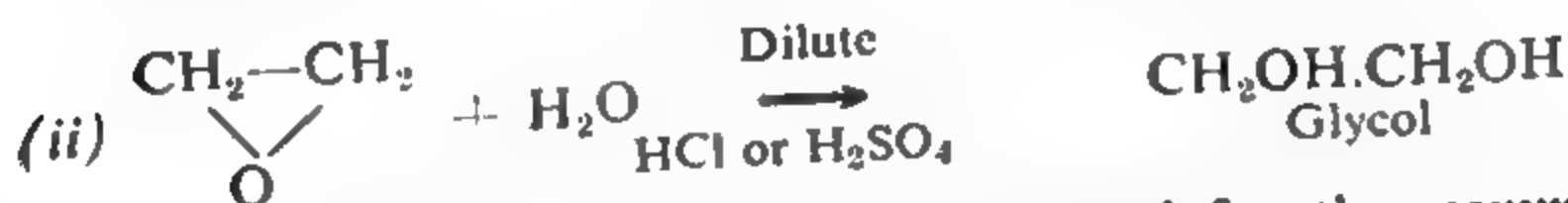
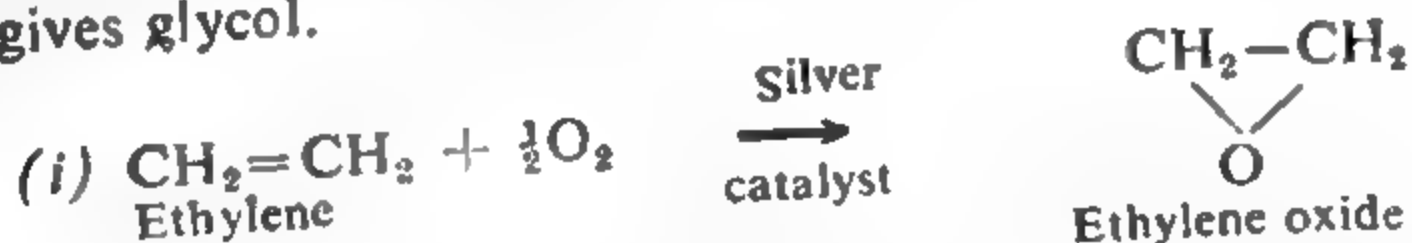
(ii) By the hydrolysis of ethylene dibromide. Ethylene dibromide when boiled with aqueous sodium carbonate solution gives glycol.



(iii) By the hydrolysis of ethylene chlorohydrin. Ethylene (from cracked petroleum) is passed into hypochlorous acid and the resulting chlorohydrin is boiled with aqueous sodium bicarbonate.



(iv) By the hydrolysis of ethylene oxide. Ethylene combines with oxygen in the presence of a 'silver' catalyst at high temperature and pressure, to give ethylene oxide which on warming with a dilute mineral acid gives glycol.

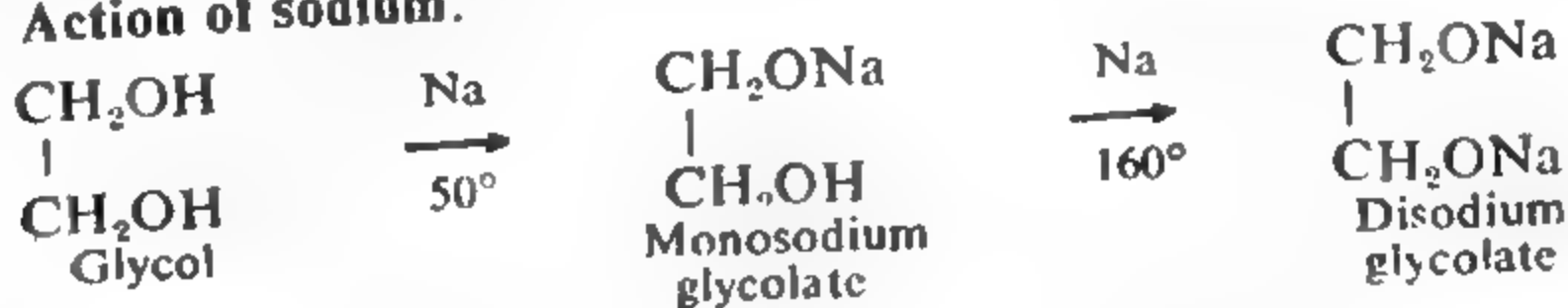


Methods numbered (iii) and (iv) are used for the commercial preparation of glycol.

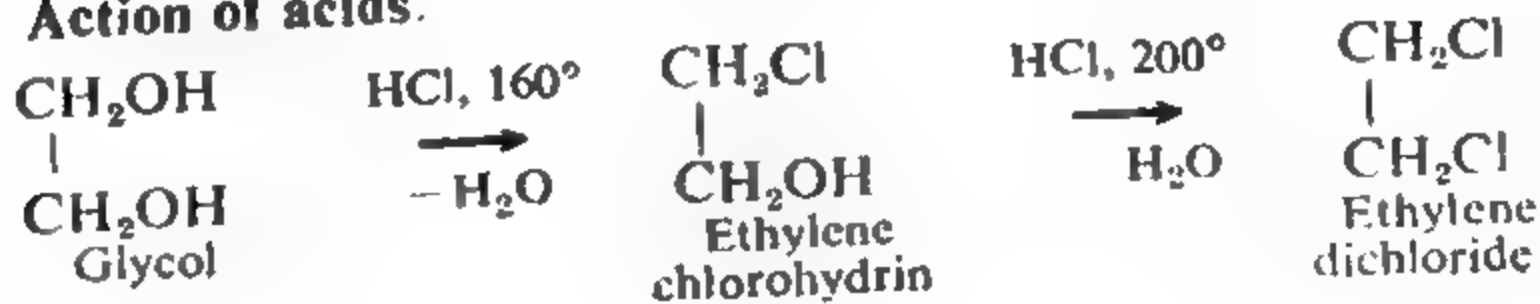
Physical Properties. Glycol is a colourless syrupy liquid boiling at 197° . It has a sweet taste. It is miscible with water and ethyl alcohol in all proportions but is immiscible with ether.

Chemical Properties. Since glycol consists of two primary alcohol groups linked together it gives all the reactions characteristic of primary alcohols. The two hydroxyl groups are attacked one after the other depending upon the conditions of reaction as illustrated below :

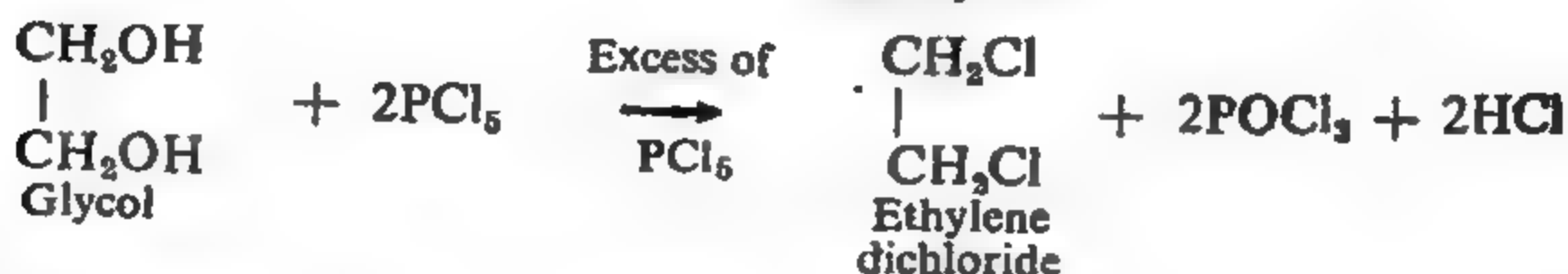
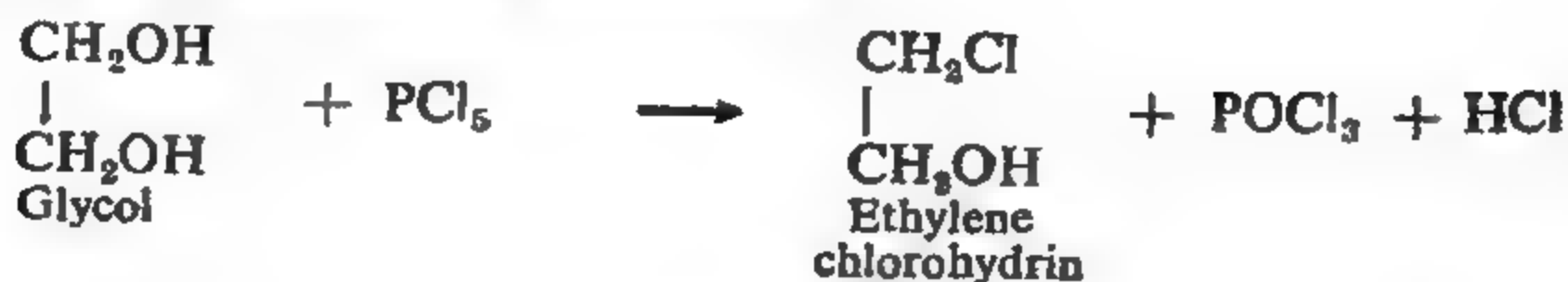
(1) Action of sodium.



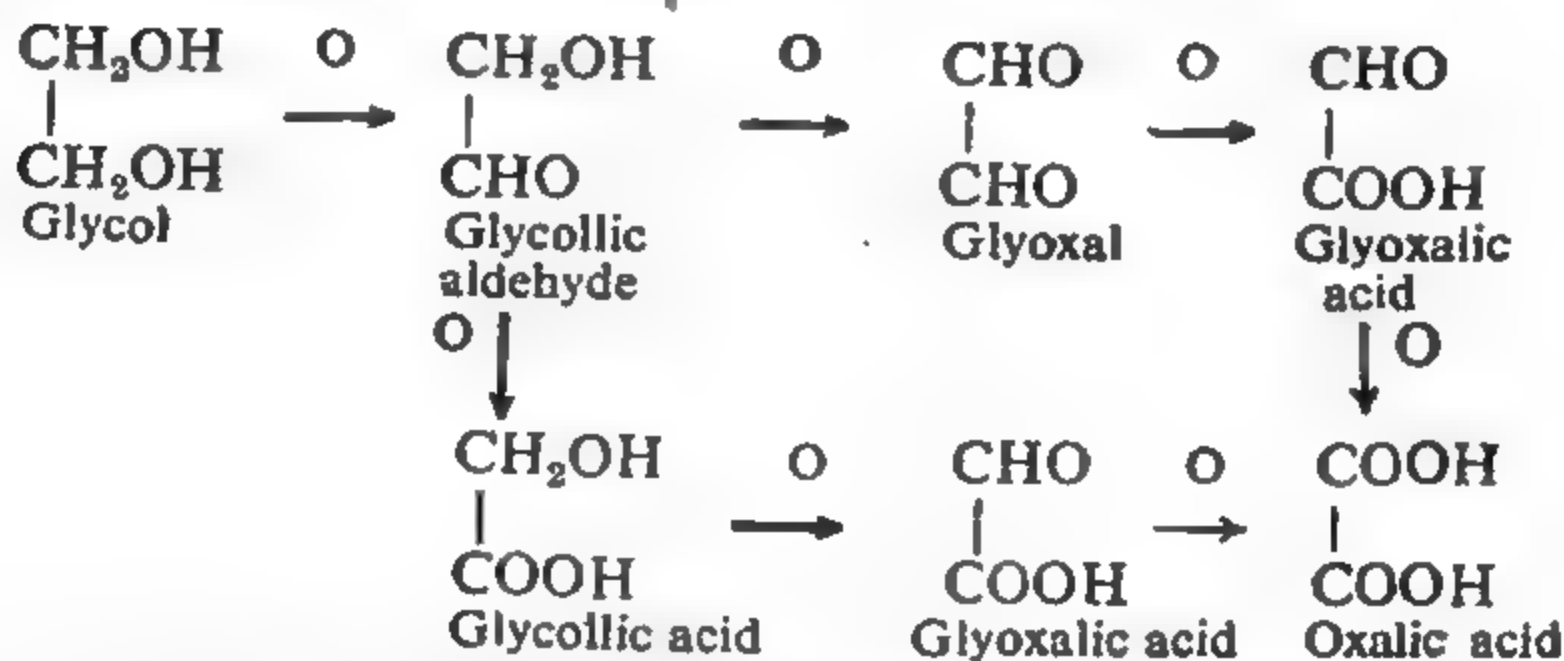
(2) Action of acids.



(3) Action of phosphorus pentachloride.

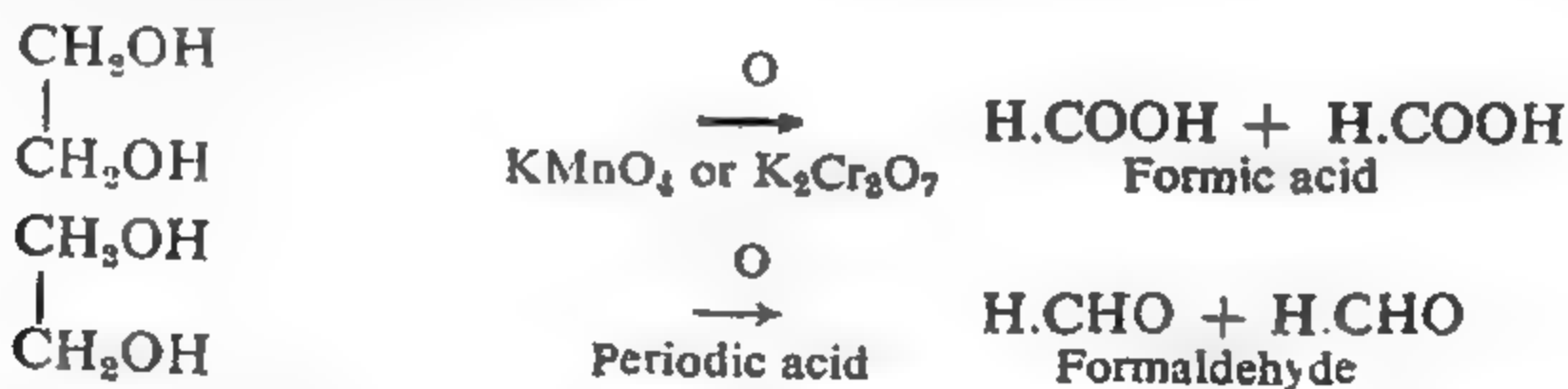


(4) Oxidation (a) With nitric acid.

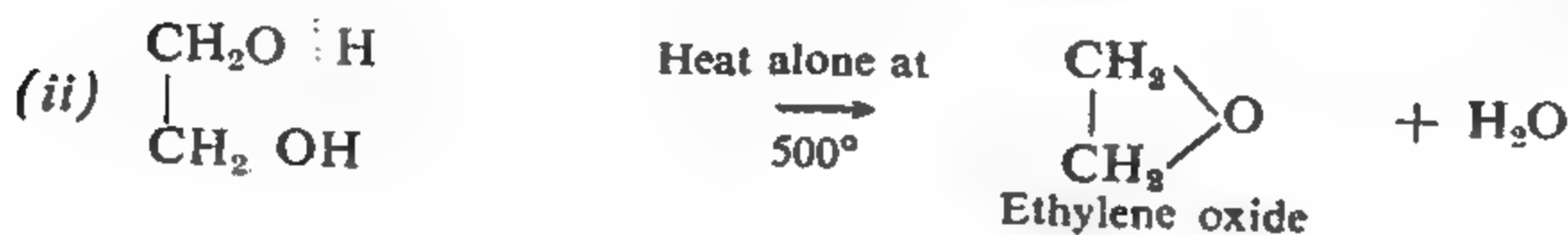
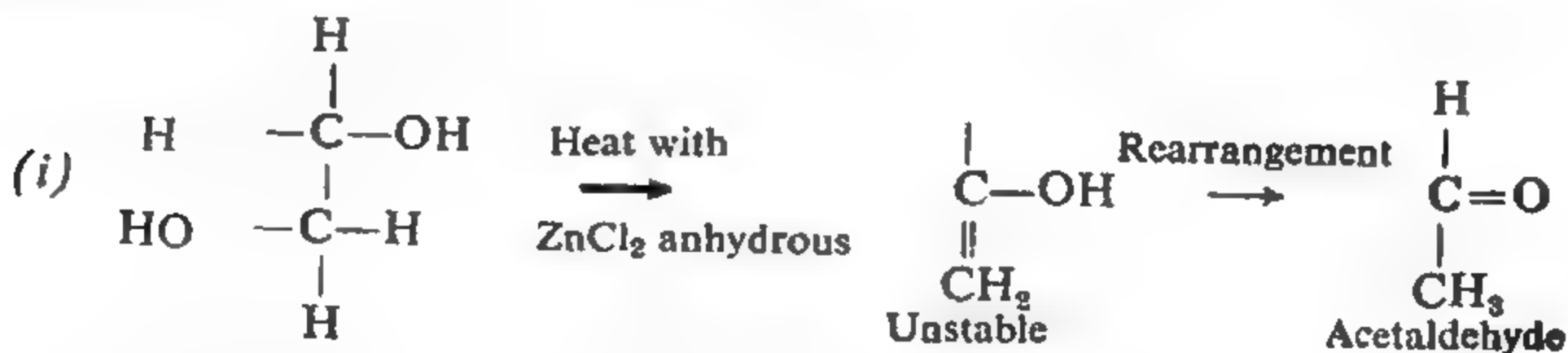


The main products of oxidation are found to be glycollic acid and oxalic acid.

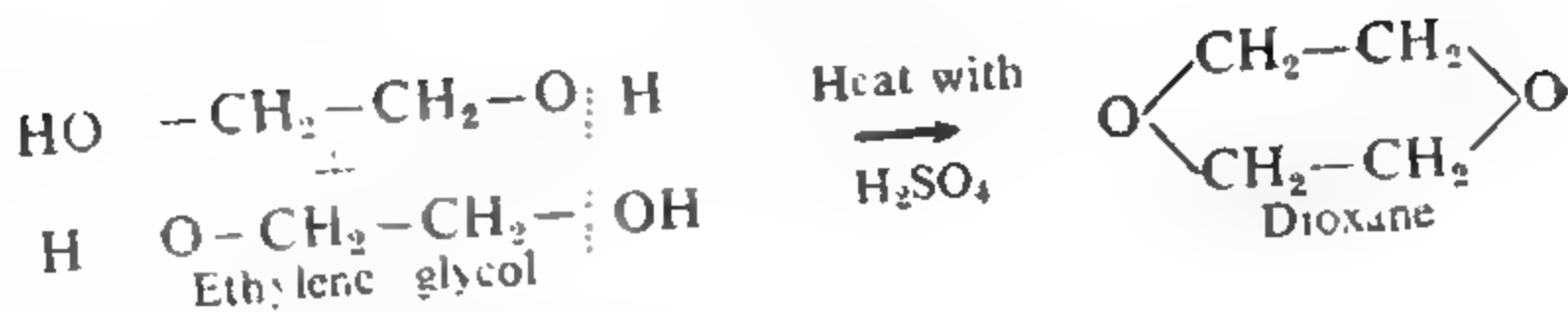
(b) With acid permanganate, dichromate, periodic acid Glycol undergoes fission as below :



(5) Dehydration. Glycol yields different products under different conditions.



(iii)



Dioxane is a very useful industrial solvent.

Uses. Glycol is used .

(1) As *antifreeze* for motor-cars and as a *cooling liquid* in air-plane motors as it forms a low freezing mixture with water. (2) For preventing ice formation on aeroplane wings. (3) For preparing *low-freezing dynamite*. (4) As a *preservative*. (5) As a *dielectric* in electrical condensers. (6) As a starting material for the production of a large number of compounds.

TRIHYDRIC ALCOHOLS

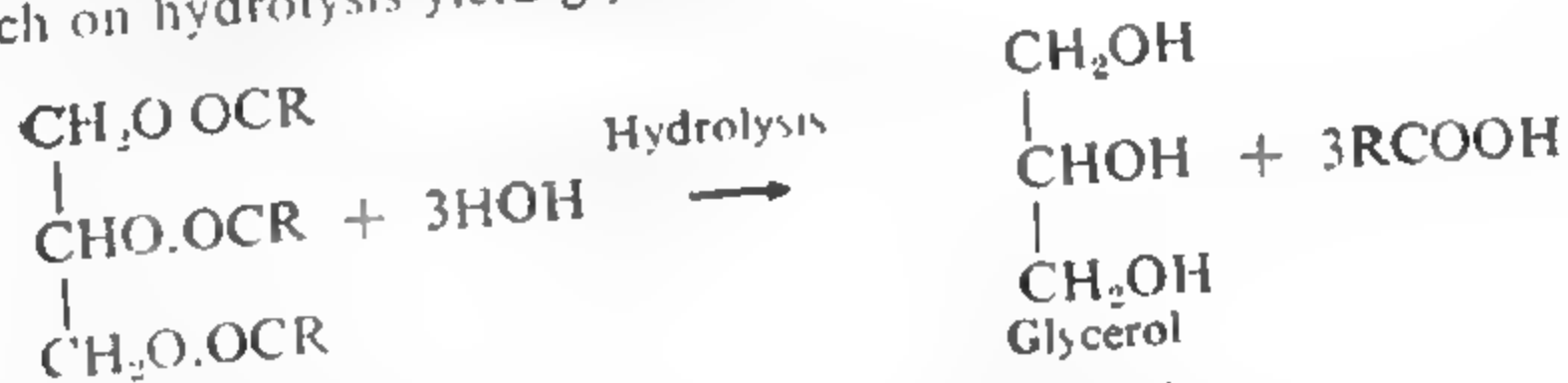
Trihydric alcohols are those which contain three hydroxyl groups, each hydroxyl group being attached to a different carbon atom. The only important trihydric alcohol is glycerol

GLYCEROL, 1, 2, 3.—PROPANE TRIOL, $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH}$.

Glycerol occurs in almost all animal and vegetable oils and fats in the form of *glyceryl esters* of higher fatty acids and unsaturated acids, mainly palmitic, stearic and oleic acids.

Manufacture.

(1) **From Oils and Fats.** Glycerol is chiefly obtained from oils and fats. As mentioned above, oils and fats are glycerides of higher fatty acids which on hydrolysis yield glycerol.

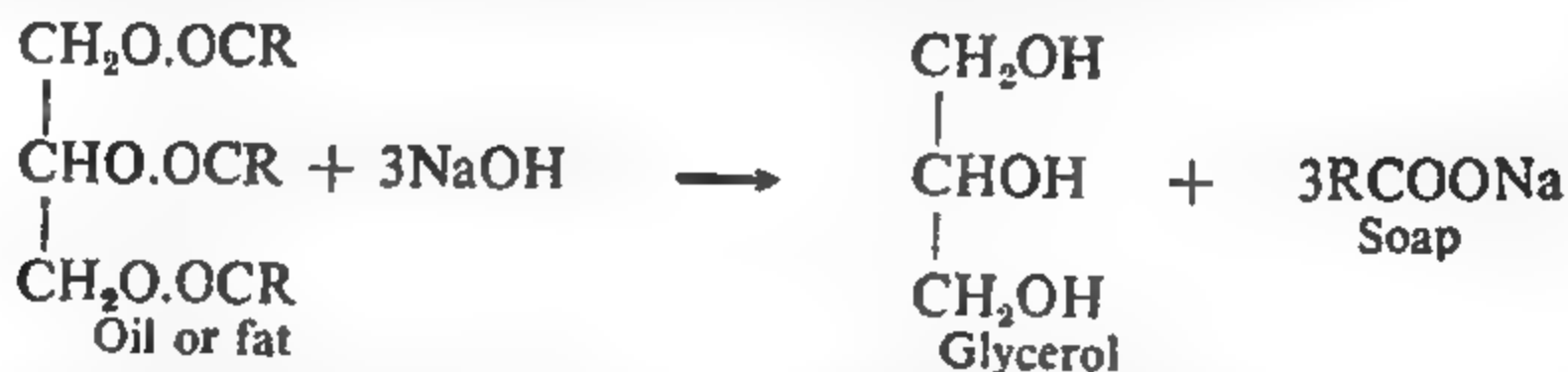


(R may be $\text{C}_{15}\text{H}_{31}-$, or $\text{C}_{17}\text{H}_{33}-$ or $\text{C}_{17}\text{H}_{35}-$)

The hydrolysis may be carried out either by sodium hydroxide, as in the manufacture of soap or by steam under pressure, as in the preparation of stearic acid for candle industry. In both the processes, glycerol is obtained as by-product.

(a) **Glycerol from soap manufacture.** Soap is prepared by hydrolysing the oils or fats with alkali solution. For this purpose, the oil or fat is boiled with excess of sodium hydroxide solution when soap is

obtained as a semi-solid mass and glycerol remains in solution.



Sodium chloride is added to salt out the soap which is removed and the remaining solution, known as the **spent lye**, is treated as below for the recovery of glycerol :

The excess of sodium hydroxide is neutralised by adding a calculated amount of hydrochloric acid or sulphuric acid. The free organic acids formed during hydrolysis are precipitated as insoluble aluminium salts by the addition of alum and filtered out. During filtration, any soap, if present, is also eliminated. The filtrate is then concentrated by heating in vacuum till the liquid contains about 50 per cent glycerol. Sodium chloride gets precipitated and is removed by filtration. The filtrate is further concentrated by heating in vacuum till the solution contains about 85 per cent of glycerol. This concentrated solution is treated with animal charcoal to adsorb any colouring matter present and then subjected to steam distillation in vacuum. The aqueous distillate is then evaporated in vacuum when perfectly colourless glycerol, which is over 99 per cent pure, is obtained.

A line sketch of the plant for the recovery of glycerol from spent lye is shown in Fig. 1.

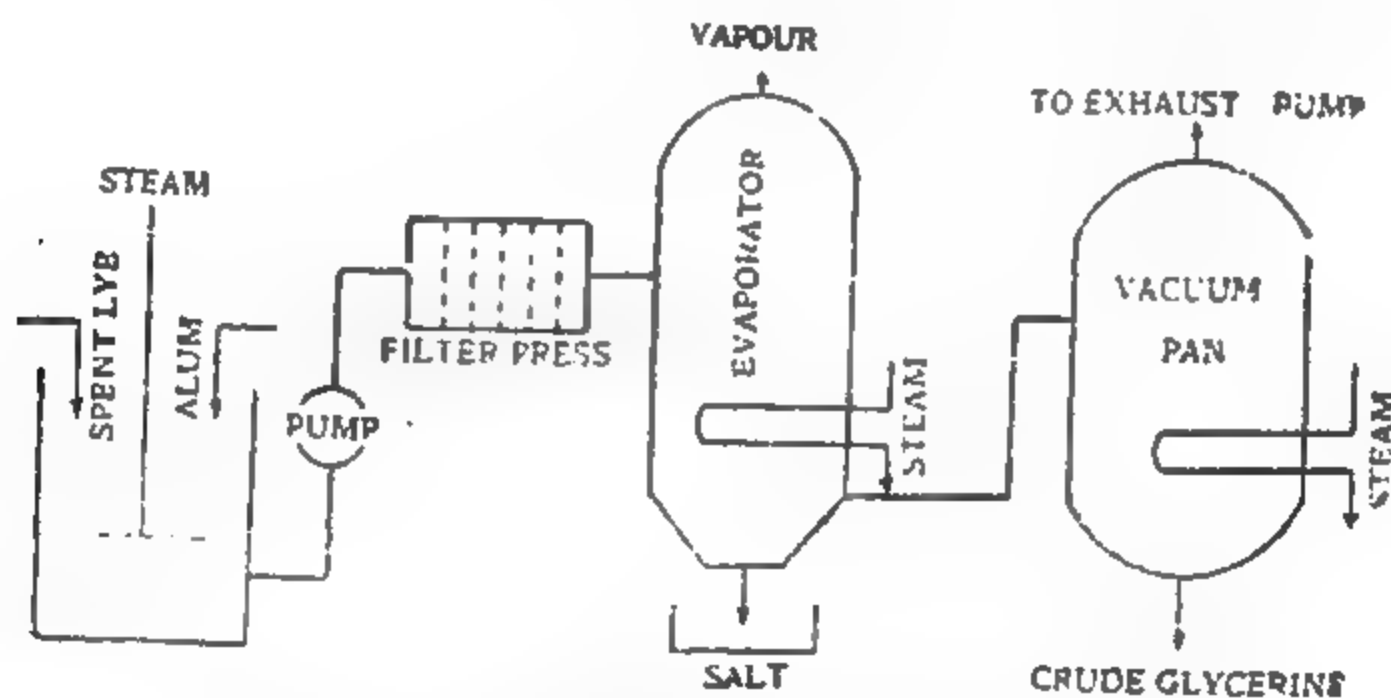


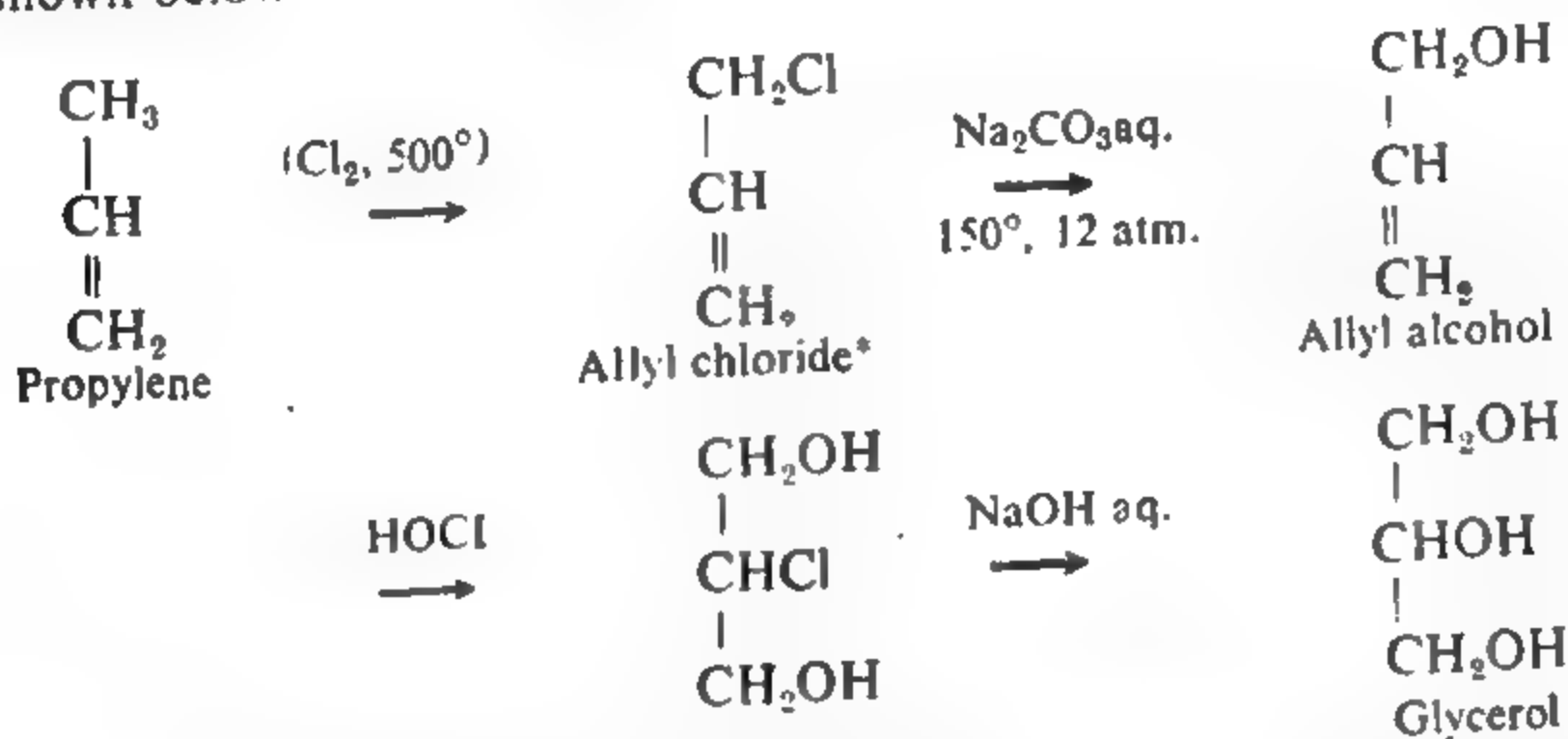
Fig. 1. Recovery of glycerol from spent lye

(b) **Glycerol from candle industry.** The stearic acid, required in candle industry for hardening the wax (so that it may not soften on heating), is obtained by the hydrolysis of oils and fats by steam under pressure in the presence of a catalyst, lime or zinc oxide. The solid stearic acid is removed and the aqueous solution of glycerol (known as sweet water) is treated as above for the recovery of glycerol.

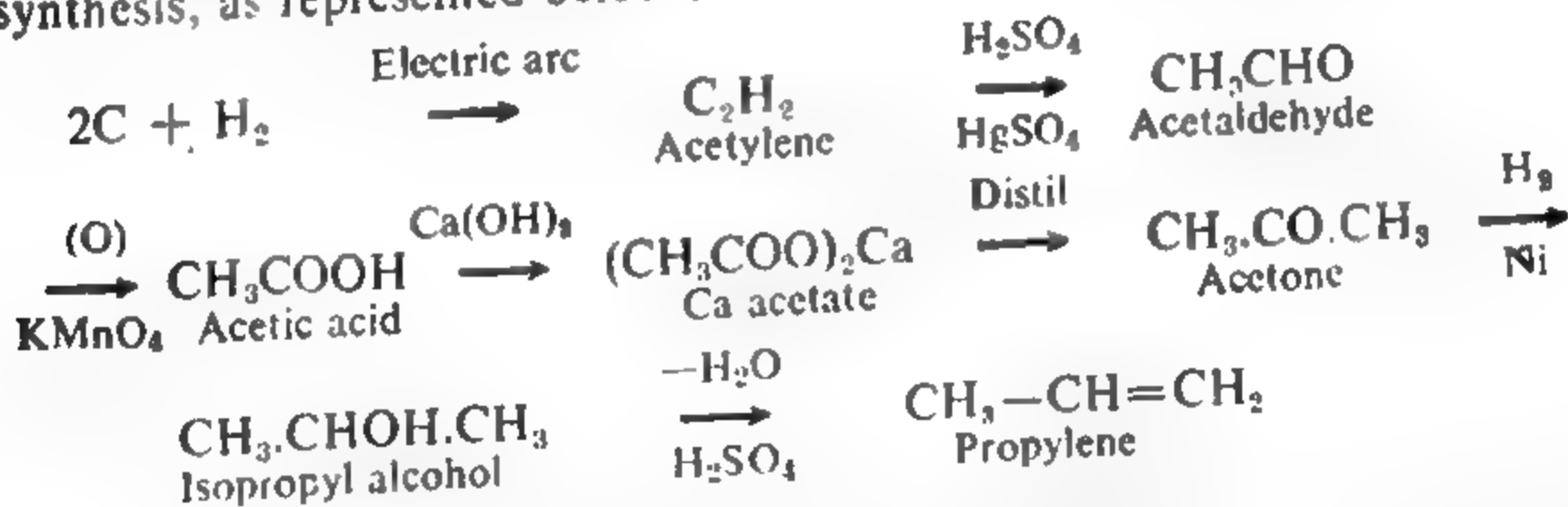
(2) **Glycerol from Sugar Fermentation.** During the alcoholic fermentation of sugar by yeast, about 3 per cent of glycerol is also produced. It has been shown that if fermentation is carried out in the presence of

sodium sulphite, the yield of glycerol goes up to about 25 per cent. By mixing sugar and sodium sulphite in the ratio of 1 : 2, the yield of glycerol can be increased to about 36 per cent of the weight of sugar used.

(3) **Synthetic Glycerol.** Large amounts of glycerol are prepared in the U.S.A. synthetically from propylene (obtained from cracked petroleum) as shown below :

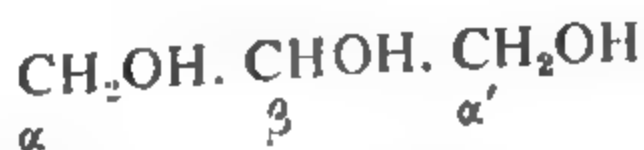


The starting material, propylene, can also be obtained from acetone (available from wood distillation) or from carbon and hydrogen by direct synthesis, as represented below :



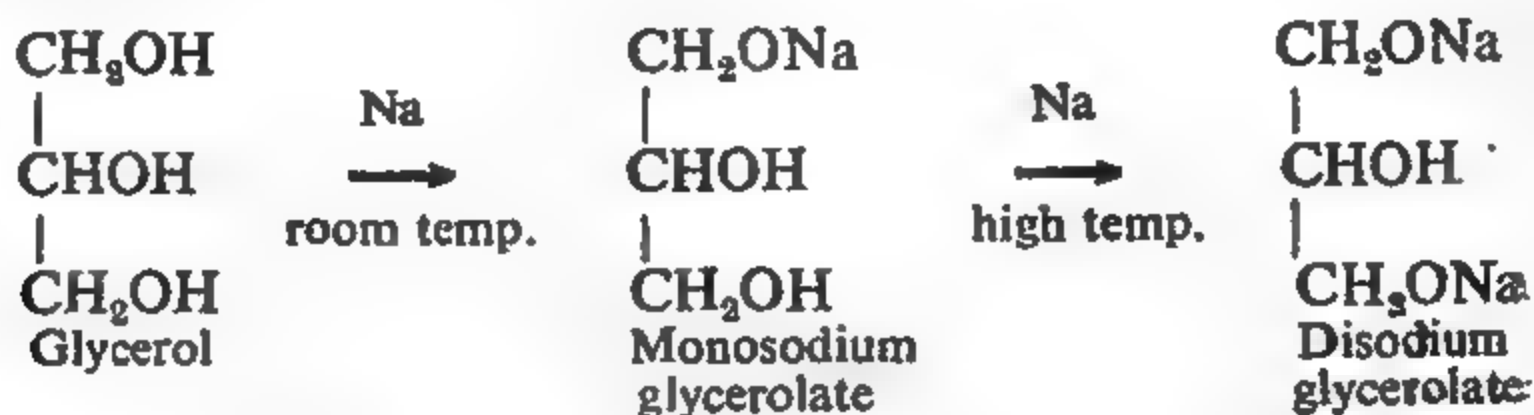
Physical Properties. Glycerol is a colourless, odourless, syrupy liquid having a sweet taste. It is miscible with water and alcohol in all proportions but is immiscible with ether and chloroform. It boils at 290° , with some decomposition. It is heavier than water (specific gravity = 1.265).

Chemical Properties. Glycerol contains one secondary and two primary alcohol groups and it gives reactions characteristic of both these groups. The carbon atoms in glycerol may be designated as α , β and α' as shown :



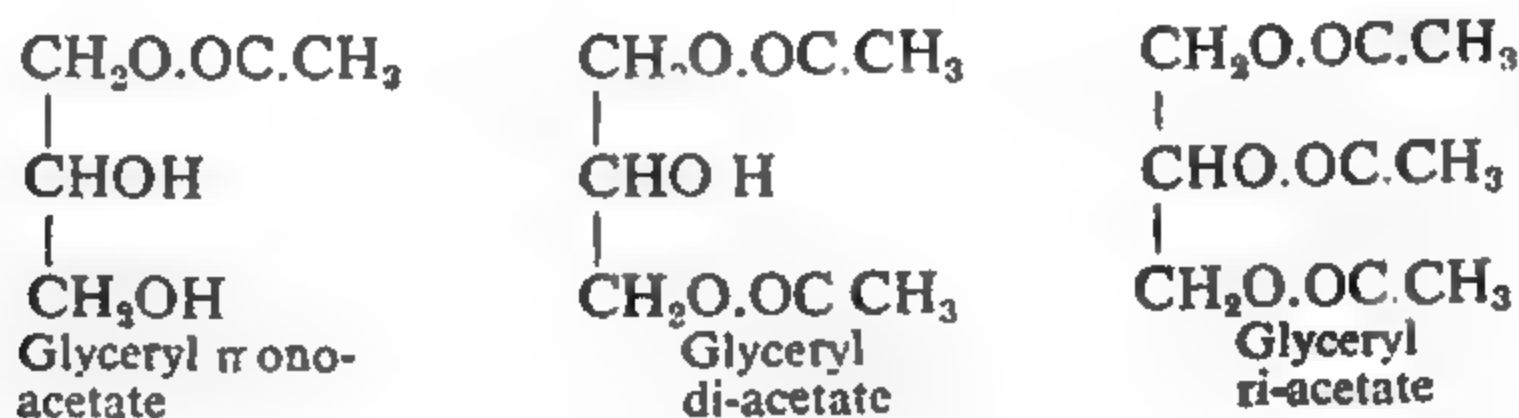
*Since the reaction is carried out at high temperature, chlorine does not add to the double bond, but instead substitutes the hydrogen atom at the saturated carbon atom.

1. **Reaction with sodium.** On treatment with sodium, α -hydroxyl group is readily attacked even at ordinary temperatures. The second, *i.e.*, α -hydroxyl group is attacked only on heating while the β -hydroxyl group is not attacked at all.



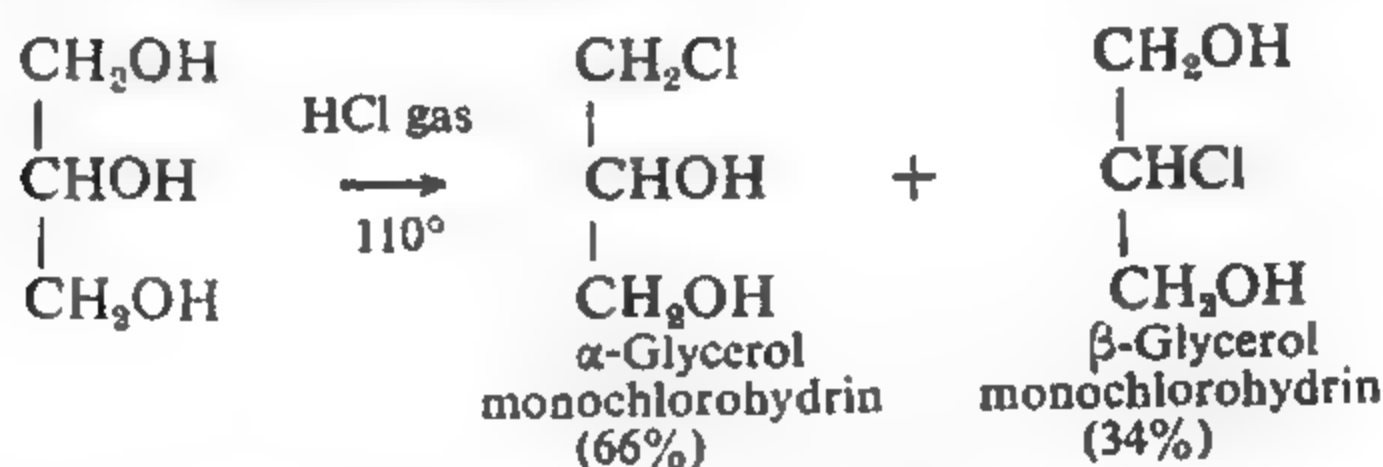
2. **Reaction with acids.** Glycerol reacts with organic as well as inorganic acids forming esters.

(i) With a mixture of acetic acid and acetic anhydride, mono, di or triesters may be obtained depending upon the amount of the acid used.

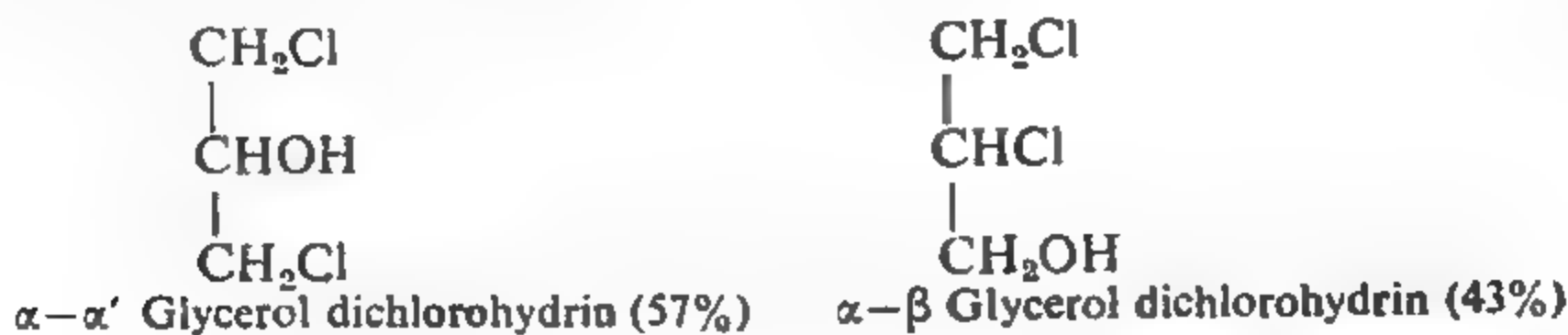


With excess of the acid and at high temperatures, the ester formed is usually the triacetate.

(ii) With hydrogen chloride at 110° , the following esters are obtained :



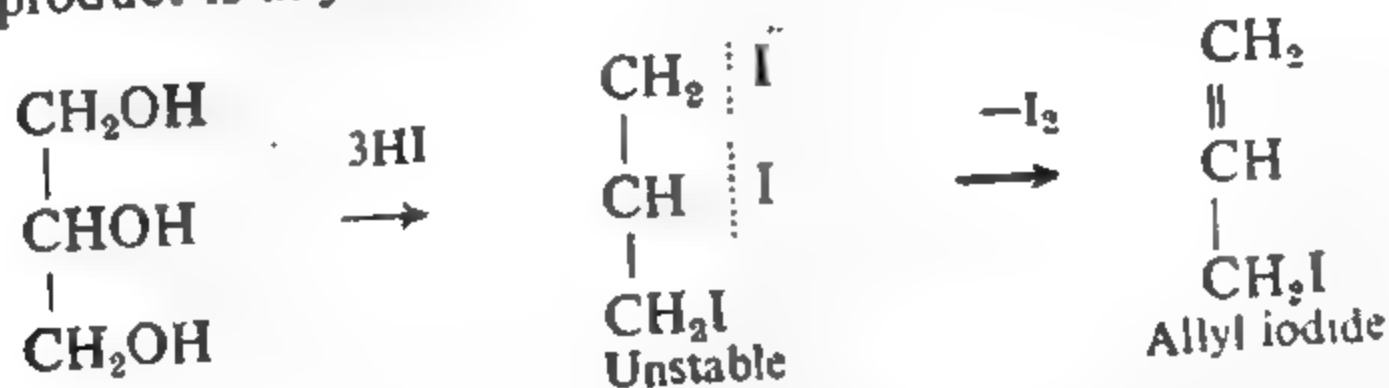
On further passing hydrogen chloride at 110° , the following products are obtained :



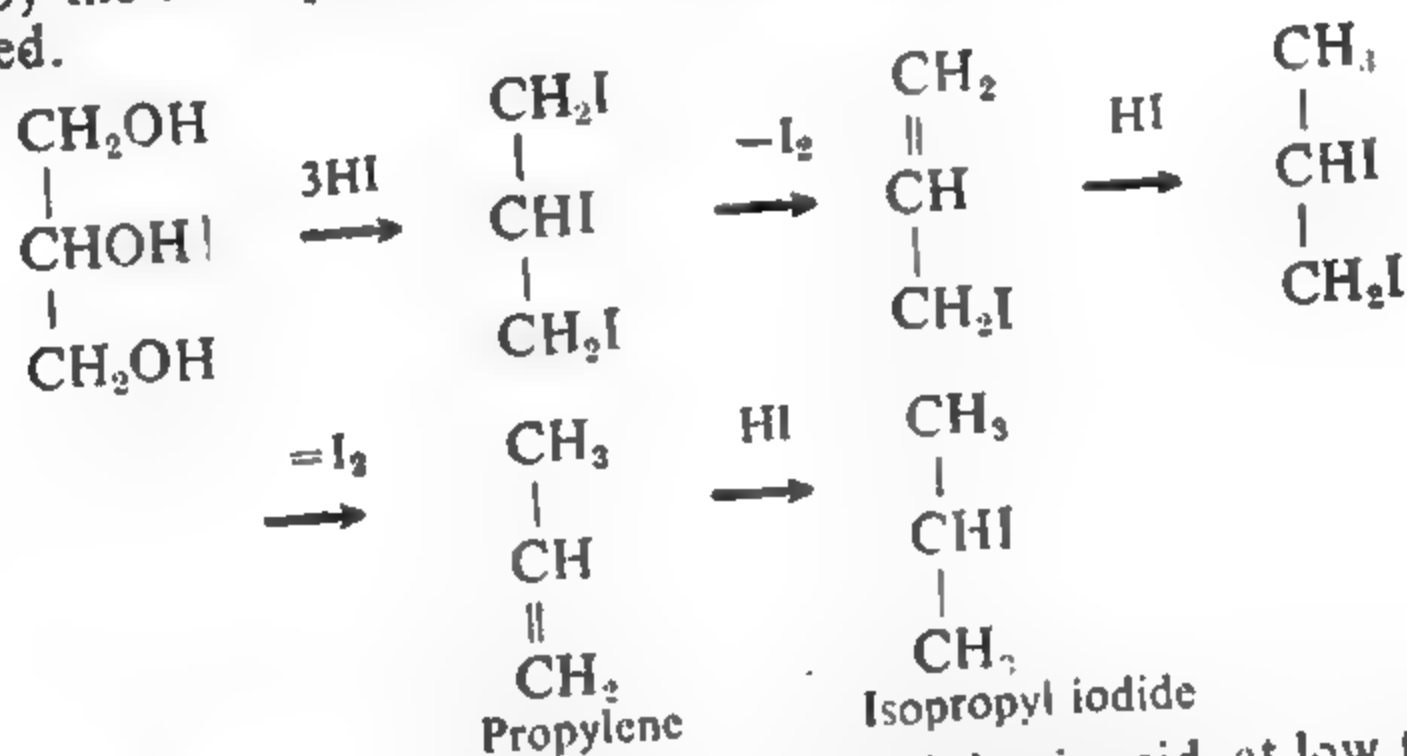
(iii) With hydrogen bromide reactions are the same as above.

(iv) With hydrogen iodide entirely different products are formed under different conditions :

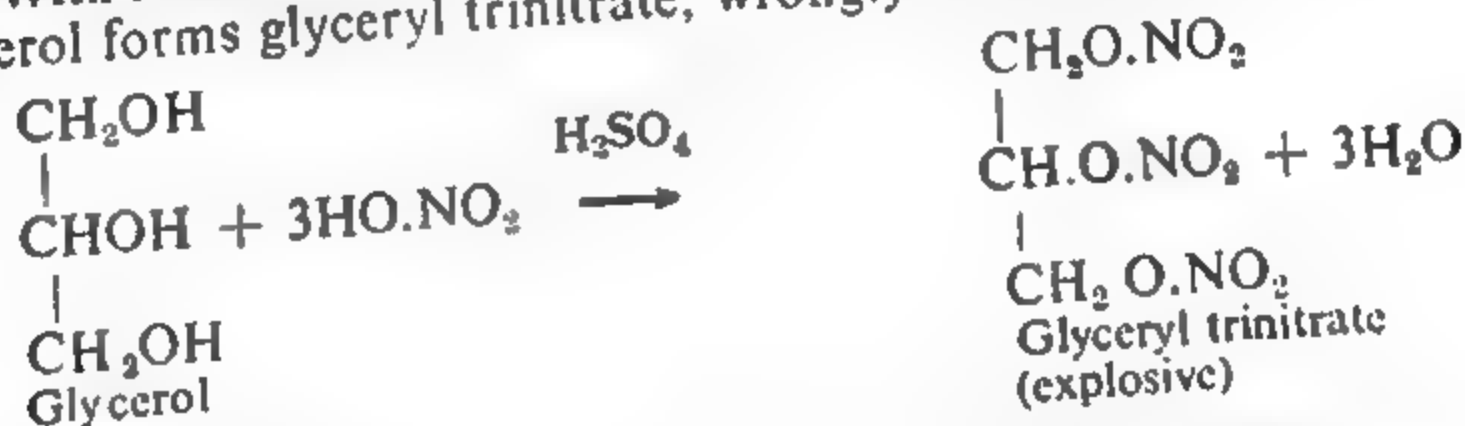
(a) When glycerol is heated with a *small amount of hydrogen iodide* the main product is *allyl iodide*.



(b) When a large amount of hydrogen iodide is used, the resulting product is mainly (80 per cent) isopropyl iodide, which, in fact, is obtained by the subsequent action of hydrogen iodide on the allyl iodide first formed.

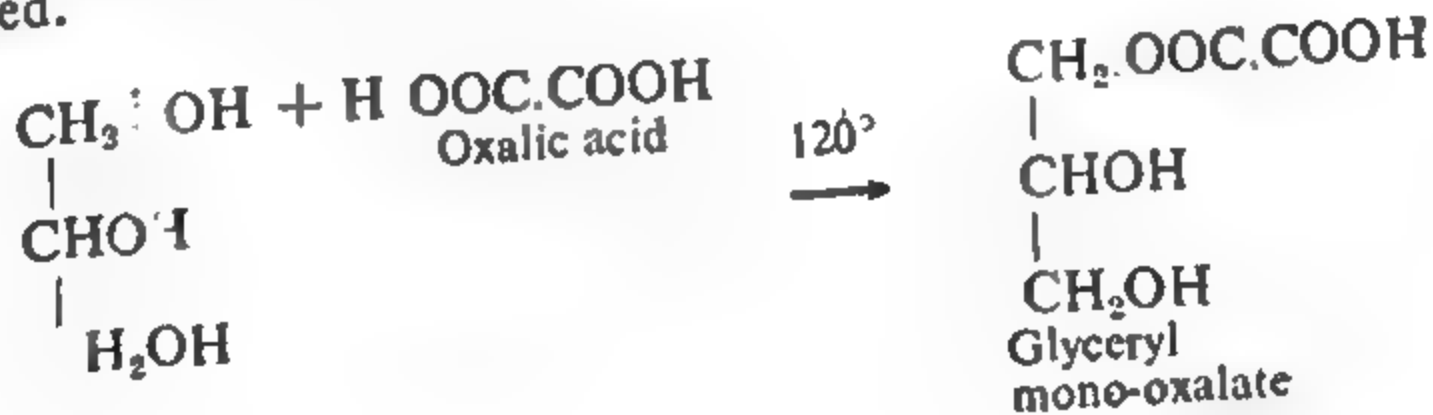


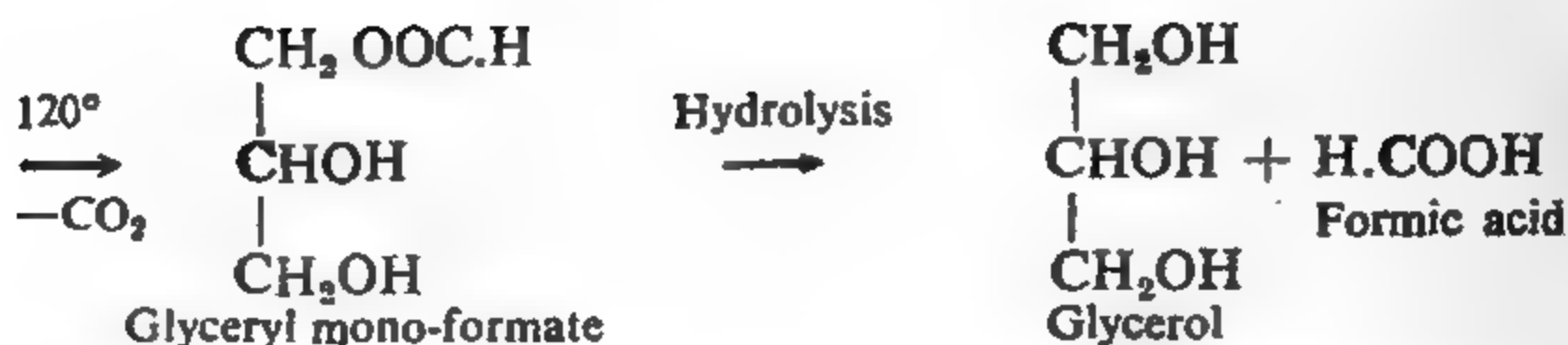
(v) With nitric acid in the presence of sulphuric acid, at low temperature, glycerol forms glyceryl trinitrate, wrongly named as nitroglycerine.



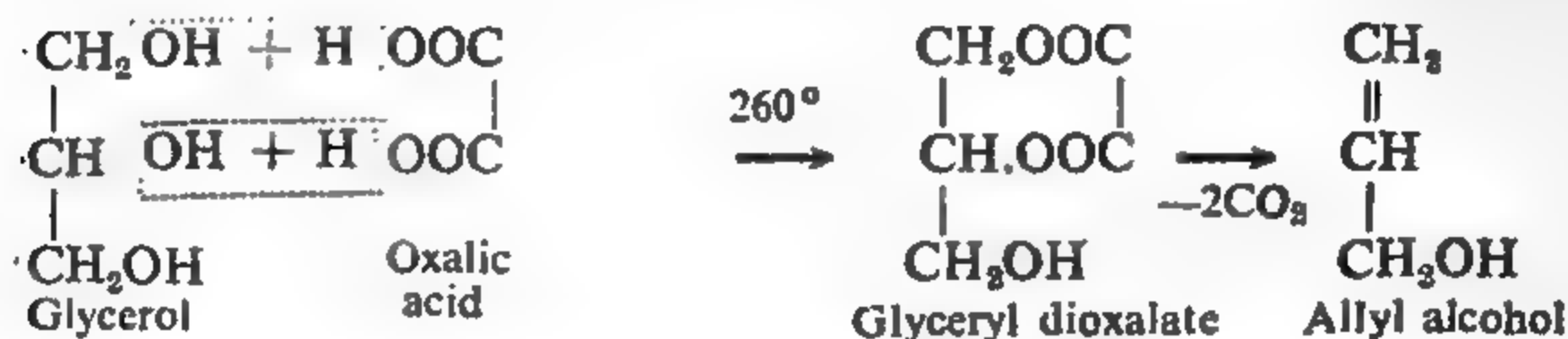
(vi) With oxalic acid, glycerol reacts in two different ways :

(a) When heated with oxalic acid to about 120° , glyceryl monoformate is obtained which on hydrolysis gives formic acid and glycerol is regenerated.

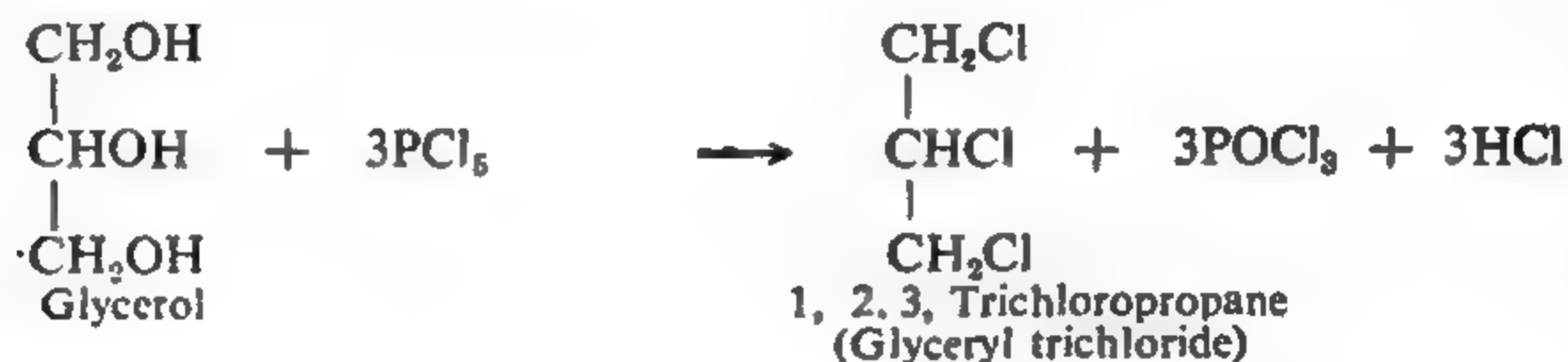




(b) When heated with oxalic acid at 260° , allyl alcohol is obtained :

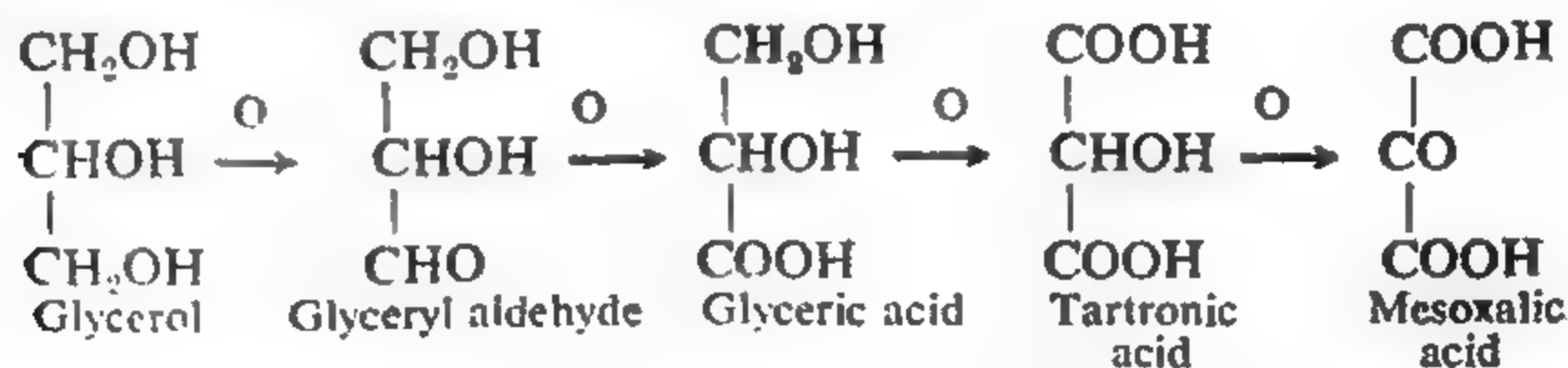


3. **Reaction with phosphorus halides.** When treated with *phosphorus pentachloride*, all the three hydroxyl groups are replaced by chlorine atoms :



Phosphorus tribromide yields glyceryl tribromide, whereas phosphorus tri-iodide behaves exactly like hydrogen iodide.

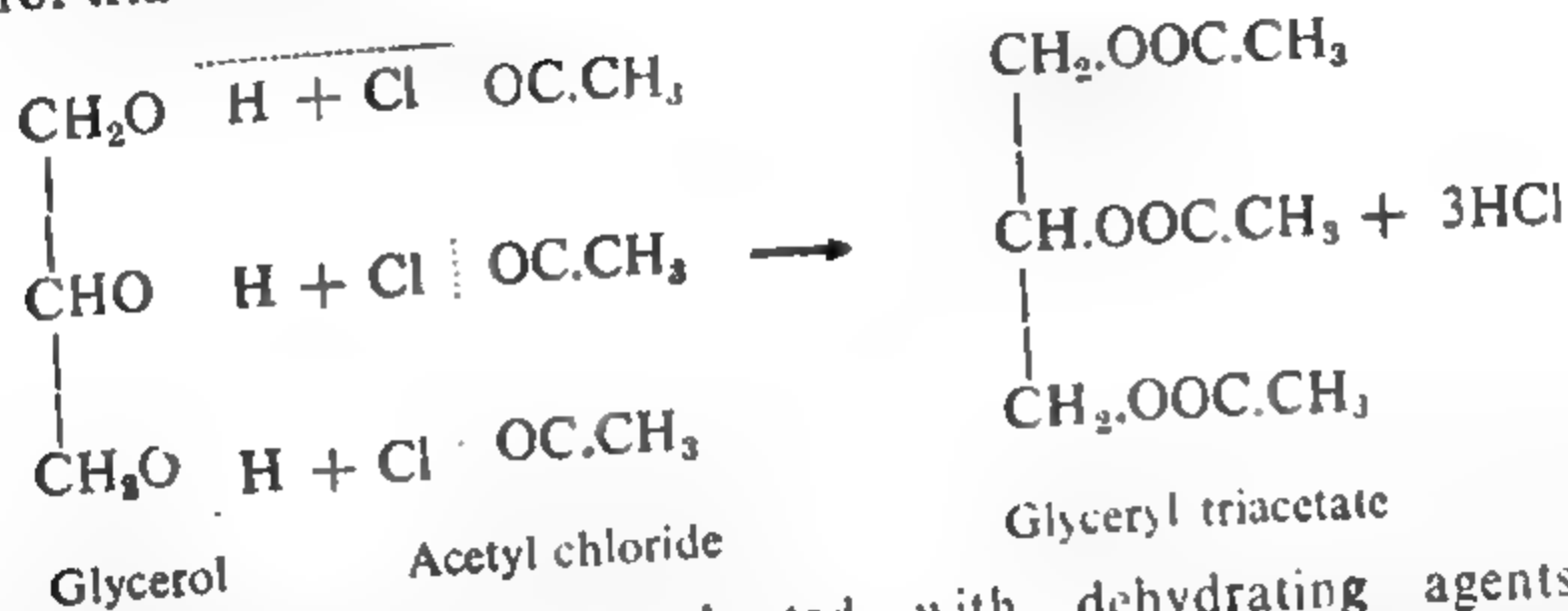
4. **Oxidation.** Glycerol yields a variety of products on oxidation depending upon the nature of the oxidising agent used. The various theoretically possible oxidation products are :



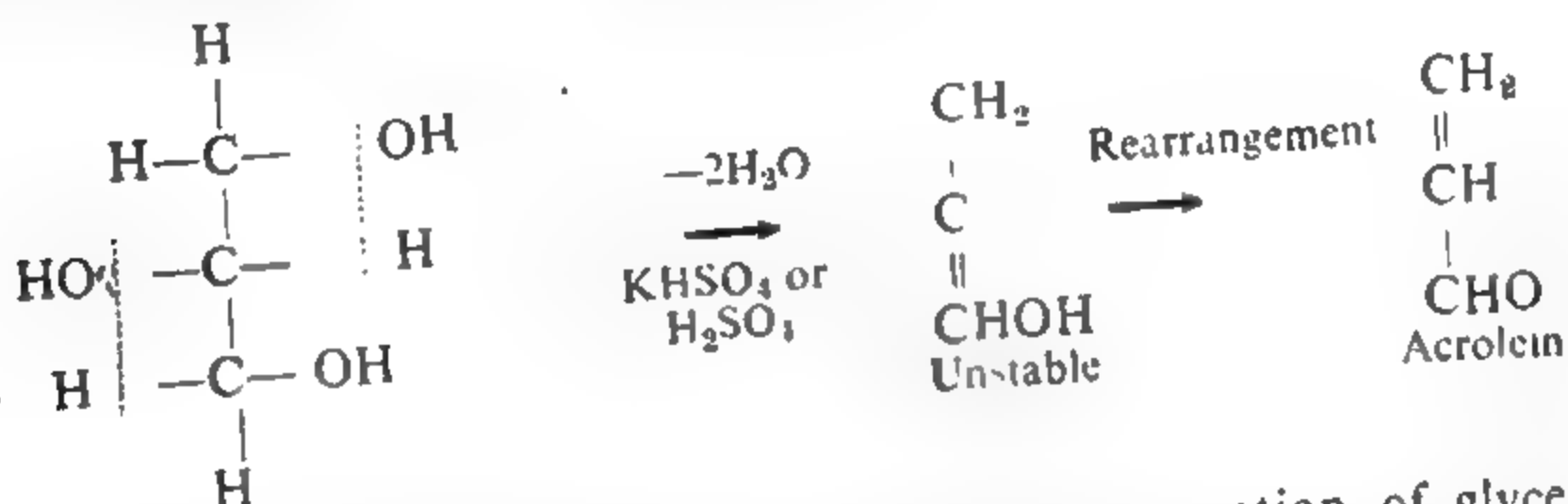
The products of oxidation will depend upon the oxidising agent used. For instance,

- (i) Dilute nitric acid gives glyceric acid and tartronic acid.
- (ii) Concentrated nitric acid yields glyceric acid.
- (iii) Bismuth nitrate produces mesoxalic acid.

5. **Acetylation.** When heated with acetyl chloride, glycerol forms glycerol triacetate.



6. **Dehydration.** When heated with dehydrating agents like sulphuric acid, potassium hydrogen sulphate, phosphorus pentoxide, glycerol gives acrylic aldehyde (acrolein).

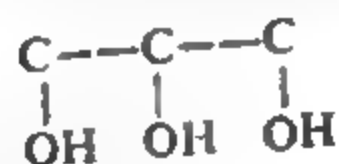


Uses. (1) The chief use of glycerol is in the preparation of glyceryl trinitrate used in making dynamites. (2) Because of its non-drying nature, glycerol is used in making non-drying printing inks, stamp colours, shoe-polish, etc. (3) Due to high viscosity, glycerol is finding use as a lubricant for watches and clocks. (4) It is also used for the manufacture of high class toilet soaps and cosmetics. (5) Glycerol finds considerable use as a preservative for food and as a sweetening agent in beverages and confectionery.

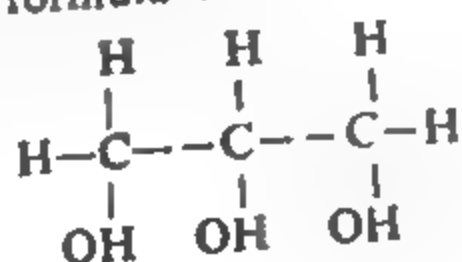
Structure. (1) The qualitative and quantitative analyses show that the molecular formula of glycerol is $\text{C}_3\text{H}_8\text{O}_3$.

(2) With acetyl chloride, it forms a triacetate, showing the presence of three hydroxyl groups in its molecule.

(3) Since not more than one hydroxyl group can be attached to one carbon atom (otherwise the compound will be unstable), glycerol will have the skeleton.

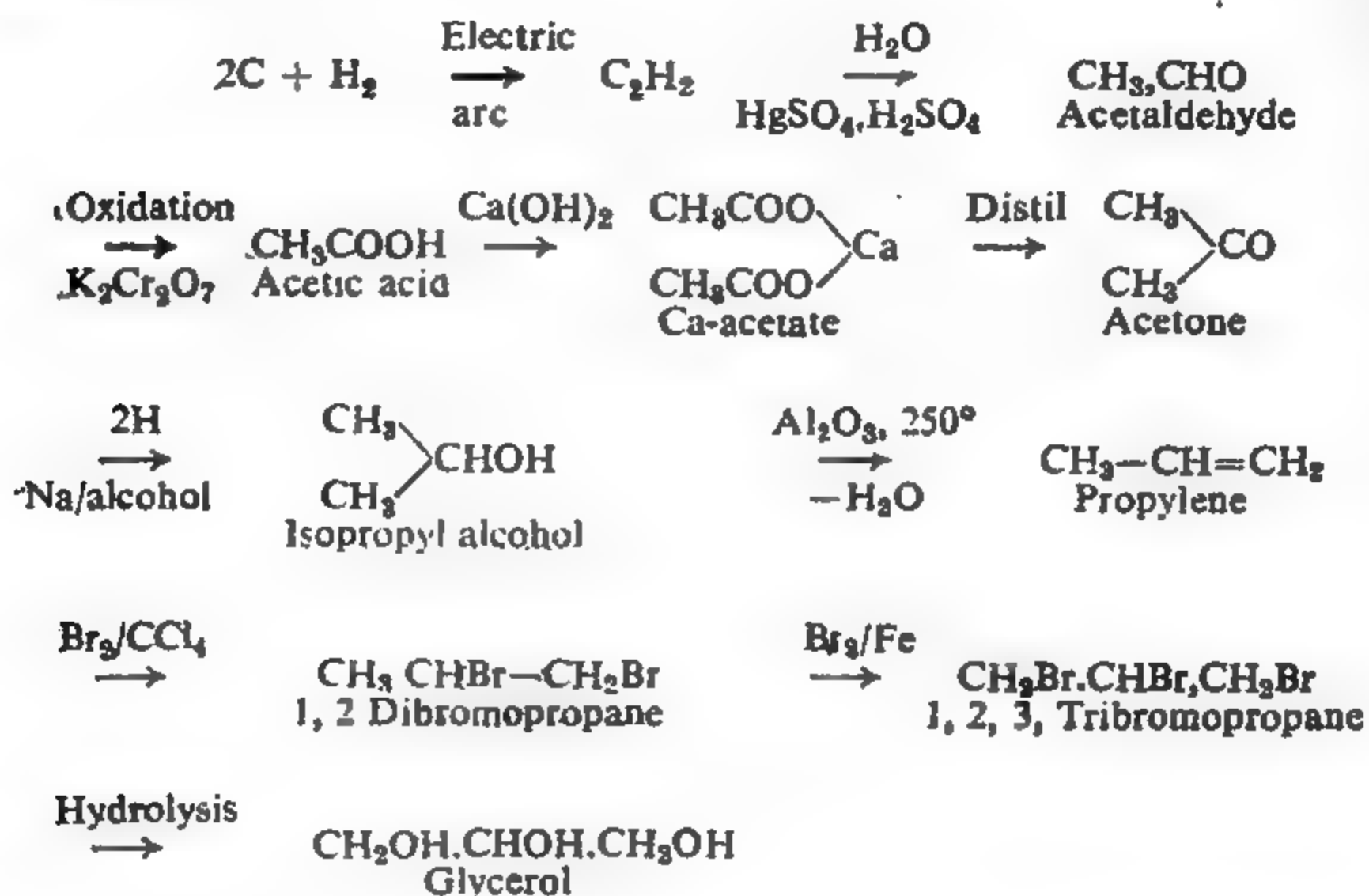


and complete structural formula will be



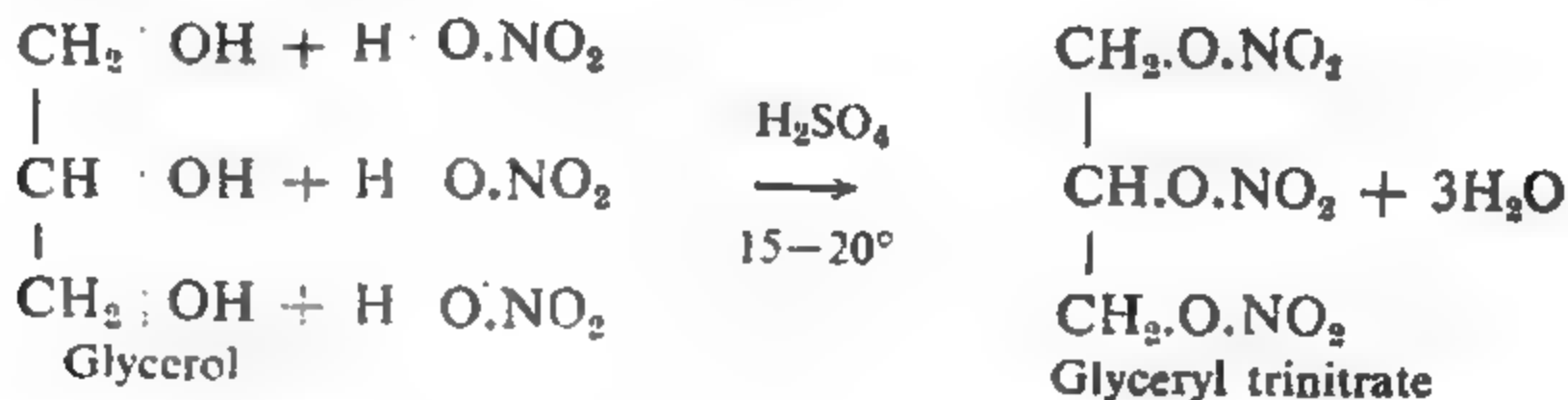
(4) This structure gets support from the fact that with phosphorus pentachloride glycerol forms the glyceryl trichloride, when each (OH) group is replaced by Cl atom.

(5) The above structure of glycerol is confirmed by its *complete synthesis*, outlined below :



Glyceryl trinitrate, 'Nitroglycerine,' $\text{C}_3\text{H}_5(\text{NO}_3)_3$.

Glyceryl trinitrate is prepared by adding glycerol in the form of a fine spray to a well cooled mixture of nitric acid and sulphuric acid, keeping the temperature below 20° .



Obviously, glyceryl trinitrate is an ester and not a nitro-compound.

When the reaction is complete, the reaction mixture is transferred to ice-cold water, when the liquid separates into two layers. The upper oily layer of glyceryl trinitrate is separated, washed with water and then with dilute sodium carbonate solution to neutralise any acids. It is finally washed with water and then filtered through a mat of sponges to eliminate any suspended impurities.

Properties. Glyceryl trinitrate is a poisonous, colourless, oily liquid, insoluble in water but readily miscible with alcohol and ether. When ignited, it burns quietly but when heated rapidly or subjected to sudden shock it explodes violently giving oxygen, nitrogen, carbon dioxide and steam.



Use (1) As an explosive. Glyceryl trinitrate is used as an explosive because of its extreme sensitiveness to shock. Nobel (1867) found, however, that glyceryl trinitrate could be stabilised by mixing it with *kieselguhr* and could be transported without any risk of explosion. Glyceryl nitrate absorbed in *kieselguhr* was given the name **dynamite**.

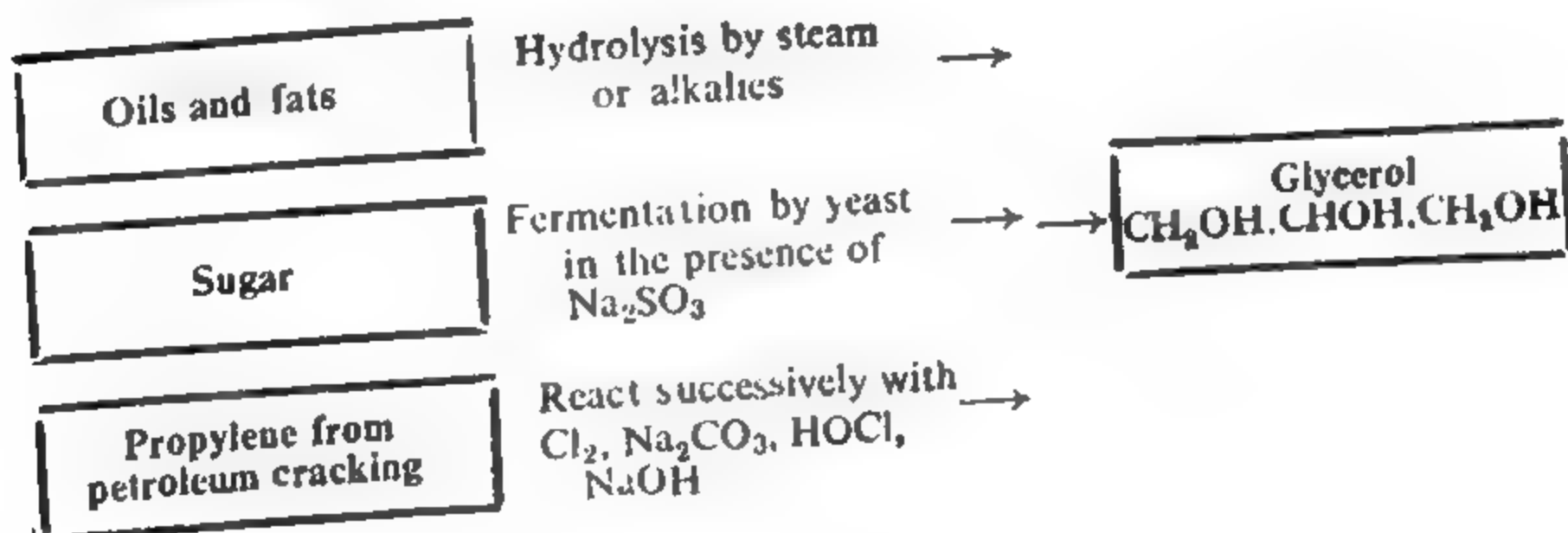
These days, dynamite is usually prepared by absorbing glyceryl trinitrate in saw-dust and adding solid ammonium nitrate to it.

The modern explosives such as *blasting gelatin* and *cordite* or *smokeless gunpowder*, are obtained by mixing glyceryl trinitrate in gun cotton and vaseline. All these explosives are extensively employed in war and peace.

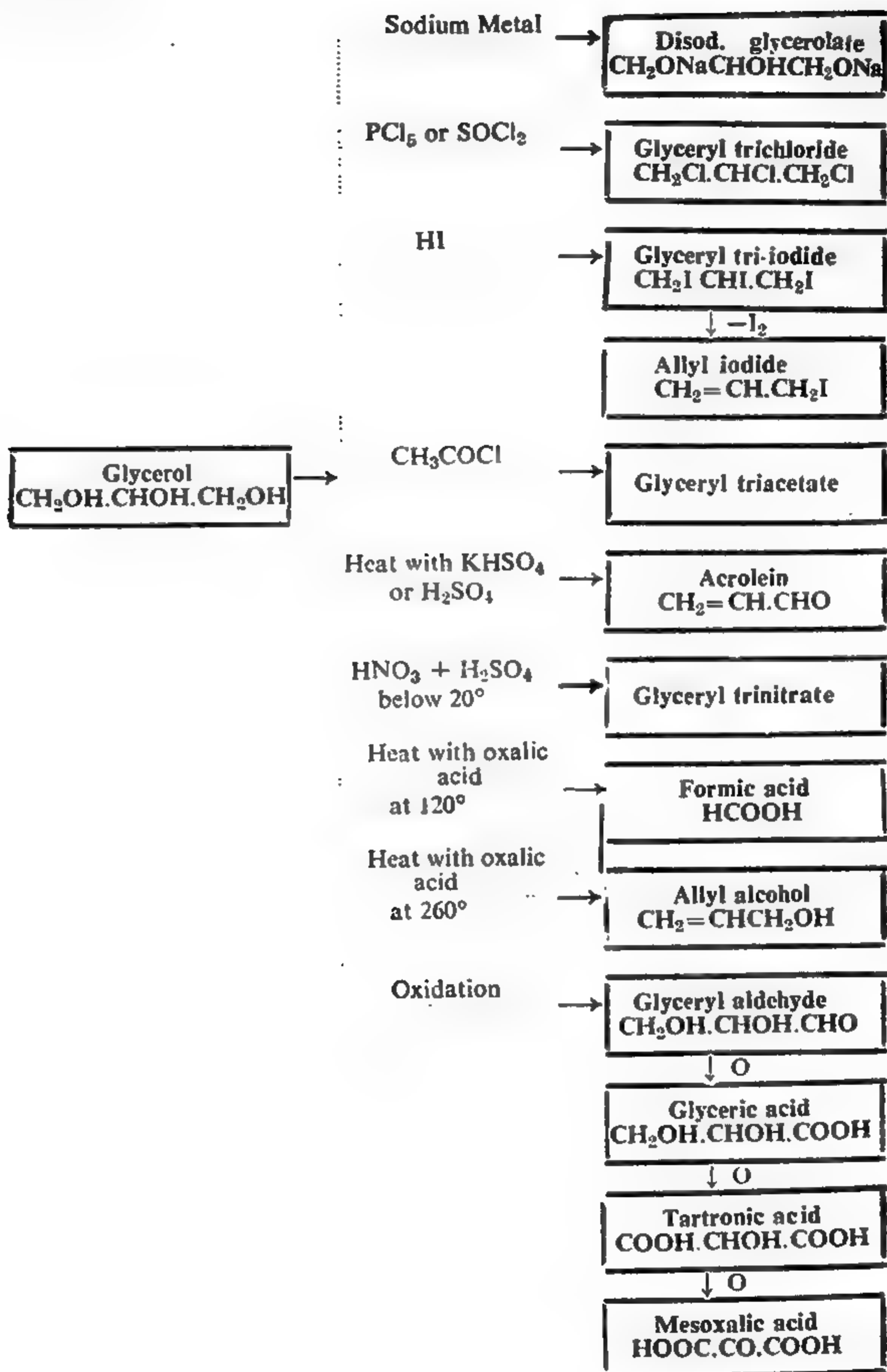
2. As a medicine. Nitroglycerine is also used in medicine in asthma, and in cases of carbon monoxide poisoning. It is also used in the treatment of a heart disease, called *angina pectoris*.

SUMMARY OF TYPICAL MEMBER

Preparation :



Properties.



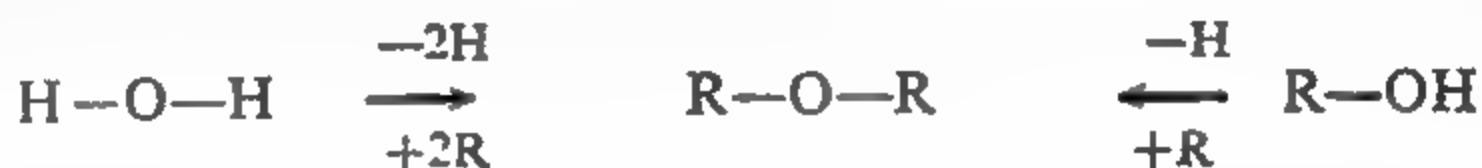
QUESTIONS

1. How is glycol prepared in the laboratory ? Give its important properties and uses.
2. How can ethylene be converted into glycol ? Describe the reactions by which the following may be obtained from glycol :
(i) Oxalic acid (ii) Succinic acid (iii) Acetylene (iv) Ethylene Chlorohydrin (v) Formic acid (vi) Dioxane (vii) Formaldehyde.
3. How is glycol manufactured ? Describe its important properties and uses.
4. How is glycol obtained from petroleum ? How does it react with :
(i) Hydrogen chloride (ii) Hydrogen iodide (iii) Oxalic acid (iv) Nitric acid and (v) Sulphuric acid.
5. How is glycerol obtained from molasses ? What products are obtained when glycerol is oxidised with :
(i) Dilute nitric acid (ii) Concentrated nitric acid (iii) Bromine water (iv) Bismuth nitrate.
6. How is nitroglycerine prepared ? Describe its important uses.
7. How is glycerol obtained from oils and fats ? How has its constitution been established ?
8. How can glycol and glycerol be synthesised from their elements ? Discuss the action of (i) Dehydrating agents (ii) Oxidising agents on glycerol.
9. Write reactions to convert Glycerol into (i) Allyl iodide (ii) Acrolein (iii) Nitroglycerine (iv) Di-sodium Glycerolate.
(Panjab Inter 1959 S)
10. (a) Give the method, represented by equations and reaction conditions, for the preparation of synthetic glycerol from a by product of petroleum industry.
(b) How does glycerol react with (i) Sodium metal (ii) Phosphorus pentachloride (iii) Oxalic acid, heated to 230°C ?
(Panjab Inter 1948)
11. Give briefly any one method for the preparation of glycerol. Prove from its reactions that it is a trihydric alcohol. What would happen if :
(a) It be added to a very cold mixture of conc. H_2SO_4 and conc. HNO_3 and
(b) if it be heated with conc. H_2SO_4 ?
(Panjab Inter 1949)
12. Give the chemistry and synthesis of glycerol from its elements. How does it react with (i) Conc. HNO_3 (ii) Oxalic acid and (iii) Conc. H_2SO_4 ?
(Panjab Inter 1948)
13. How is glycerol obtained from fats and oils ? What happens when it is (a) heated with KHSO_4 (b) treated with hot HI (c) oxidised (d) reacted with a mixture of HNO_3 and H_2SO_4 ?
(Panjab Inter 1946)
14. Draw a flow sheet diagram for the recovery of glycerine from spent lye. Briefly explain the function of each part of the manufacturing plant.
What is the action of the following upon glycerine :
(1) Na (2) HI (3) HNO_3 (in the presence of fuming H_2SO_4) (4) Acetic anhydride (5) Heating with KHSO_4 .
(Panjab T. D. C. Part I 1953)

CHAPTER XXXIII

ETHERS

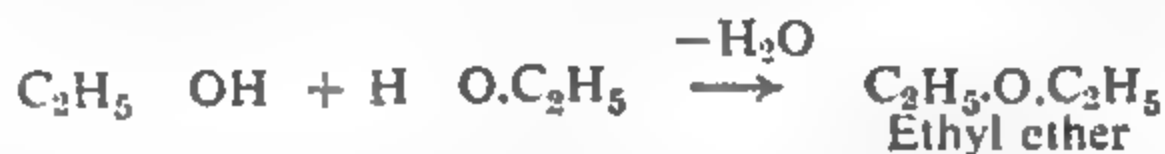
Ethers are compounds having the general structure $R-O-R'$ and may be considered as the *dialkyl derivatives* of water or better as the alkyl derivatives of alcohols in which the H atom of OH group is replaced an alkyl radical.



Because of their similarity in structure with metallic oxides, ethers can be regarded as *alkyl oxides*, e.g.,



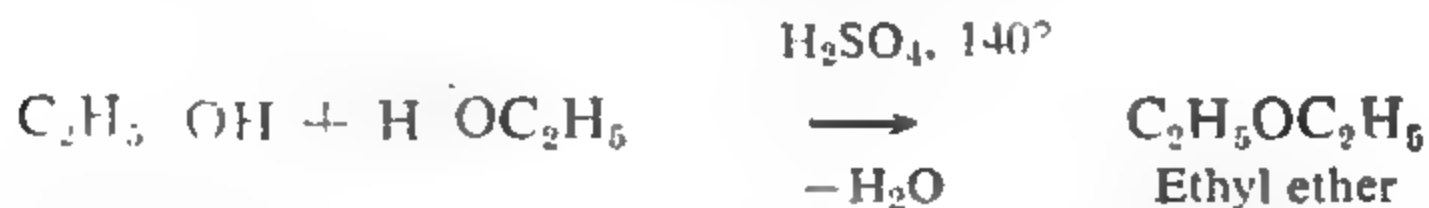
Ethers could also be looked upon as *anhydrides of alcohols* :



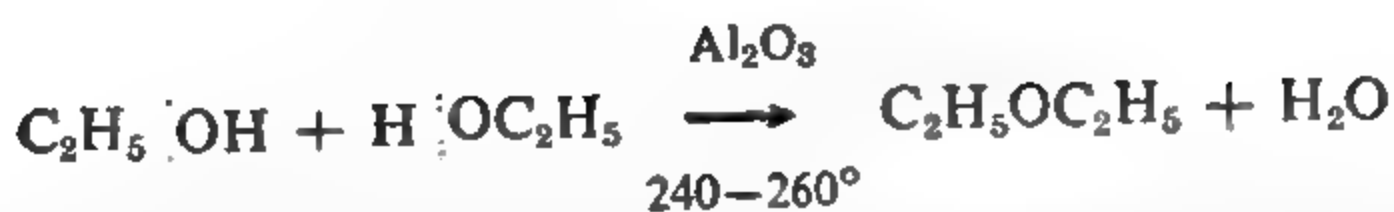
When the two alkyl groups in an ether are the same, we have a *simple* ether, e.g., $C_2H_5-O-C_2H_5$, diethyl ether. If the two groups are different, the ether is said to be *mixed*, e.g., $CH_3-O-C_2H_5$, ethyl methyl ether.

General Methods of Preparation. Ethers may be prepared by the following general methods :

(1) By the dehydration of alcohols. (i) *With sulphuric acid or glacial phosphoric acid.* Excess of alcohol, when heated with concentrated sulphuric acid or glacial phosphoric acid, loses a molecule of water from two molecules of alcohol forming ether, e.g.,

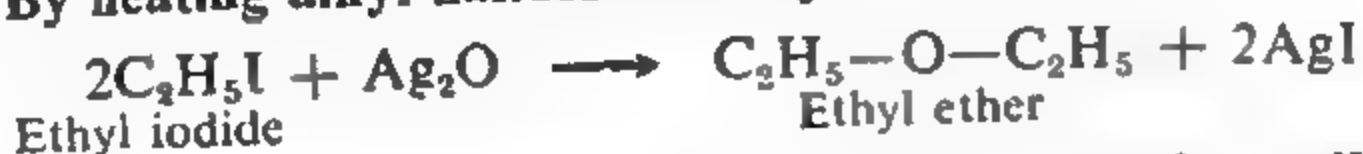


(ii) *Catalytic dehydration.* Vapour of primary alcohols, when passed over alumina at $240-260^\circ$, lose water to give ethers, e.g.,



This method is limited only to the dehydration of primary alcohols; secondary and tertiary alcohols have a strong tendency to lose water to form olefins, under these conditions.

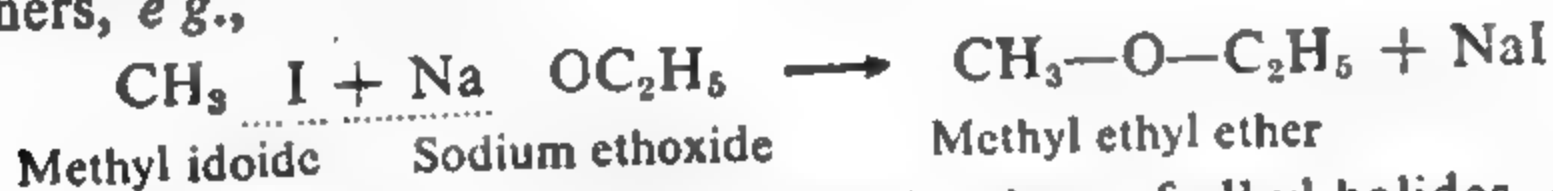
(2) By heating alkyl halides with dry silver oxide, *e.g.*,



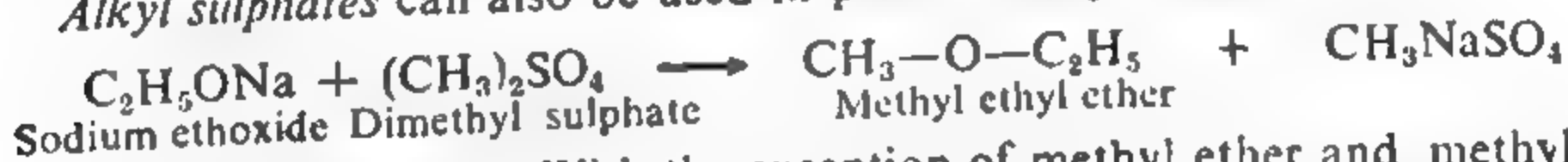
(3) By heating alkyl halides with sodium or potassium alkoxides, *e.g.*,



This method was introduced by Williamson and is known as **Williamson's synthesis**. The method is particularly useful for preparing mixed ethers, *e.g.*,



Alkyl sulphates can also be used in place of alkyl halides, *e.g.*,



Physical Properties. With the exception of methyl ether and methyl-ethyl ether, both of which are gases under ordinary temperatures, all ethers are colourless, volatile liquids with a pleasant odour.

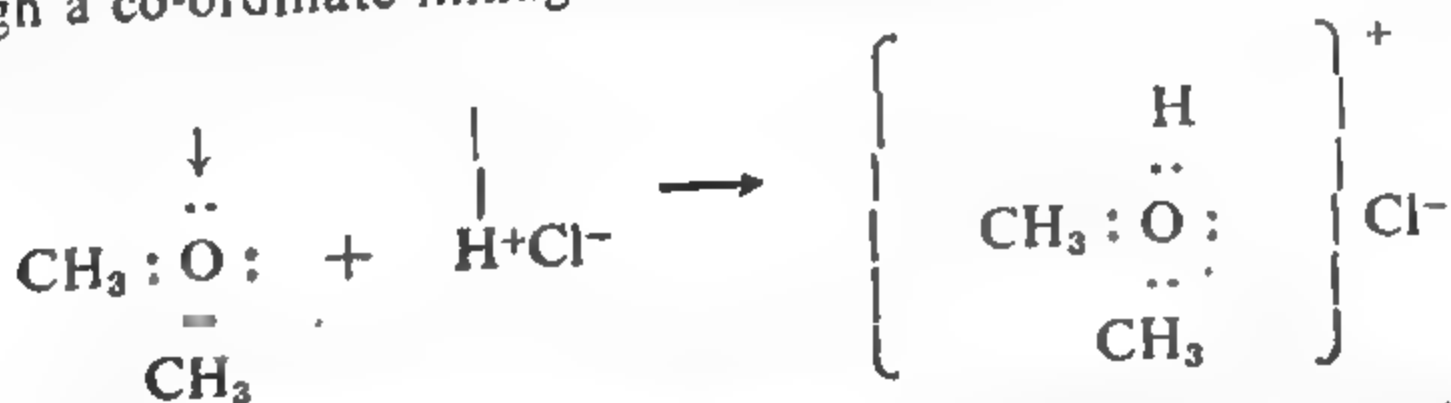
Chemical Properties. Ethers are comparatively inert substances and do not ordinarily react with reagents like alkali metals, alkalies, dilute acids, potassium permanganate and dichromate.

The important reactions of ethers are :

1. **Formation of oxonium salts.** Ethers are basic in the sense that they form stable salts with strong inorganic acids. These salts are comparable to ammonium salts $[\text{NH}_4^+]\text{X}^-$, and hence are named as *oxonium salts*, *e.g.*,



The proton (H^+) of the acid gets attached to the oxygen of the ether through a co-ordinate linkage as illustrated below :



The oxonium salts are stable only in a strongly acidic medium.

2. **Formation of peroxides.** Ethers are not oxidised by reagents like potassium permanganate and dichromate but on prolonged contact with air or ozone, they form peroxides.



These peroxides are unstable and are liable to decompose with explosive violence, on heating. Hence, before distilling an ether, the absence of any peroxide in it must be ensured.

3. **Hydrolysis.** On heating with dilute sulphuric acid under pressure, ethers are hydrolysed to the corresponding alcohols, *e.g.*,



4. **Action of halogen hydracids.** Ethers are readily attacked by concentrated hydriodic or hydrobromic acid, the final products depending upon the temperature employed.

(i) *When treated in the cold*, they are split up into an alcohol and alkyl halide :



In the case of a mixed ether, the iodine atom is attached to the smaller radical.

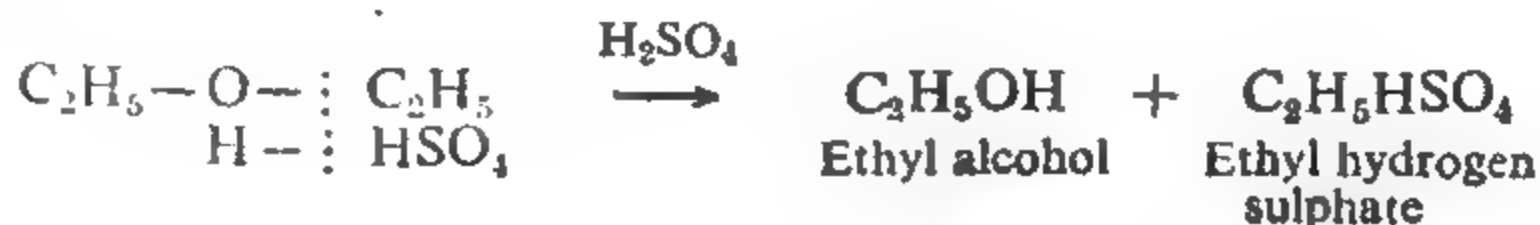


(ii) *When treated with excess of the halogen acid at high temperature*, alkyl halide and water are formed.

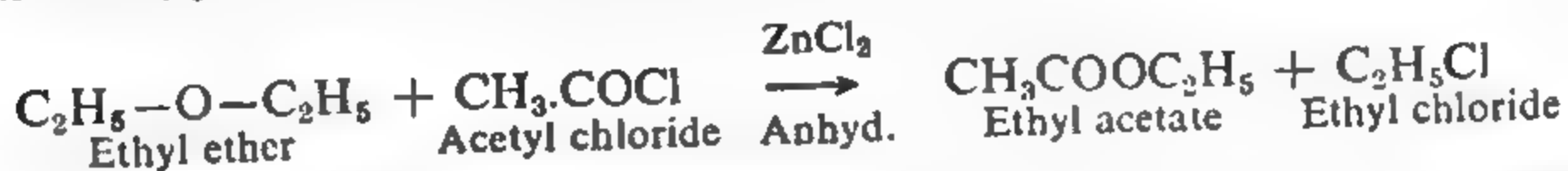


The above reactions are useful for determining the structure of ethers.

5. **Action of sulphuric acid.** In cold, ethers only dissolve in sulphuric acid forming oxonium salts as already described. If this solution is heated, the ether is decomposed to give a molecule of alcohol and alkyl hydrogen sulphate.

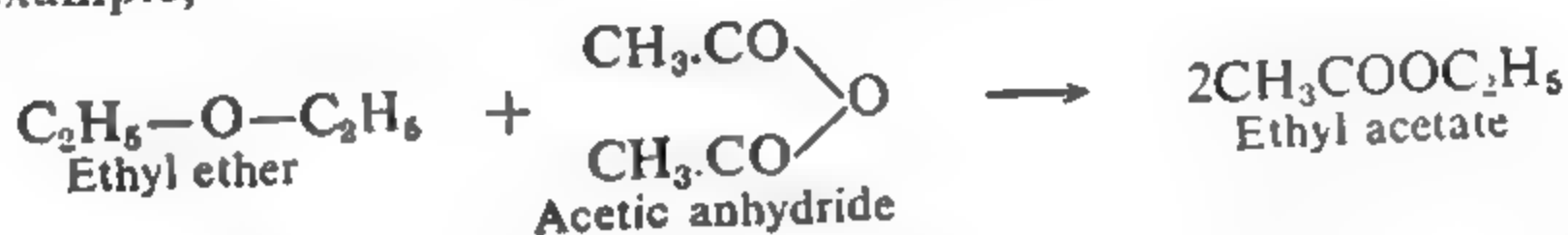


6. **Reaction with acid chlorides and acid anhydrides.** Ethers when heated with acid chlorides in the presence of anhydrous zinc chloride or alumina, yield alkyl halides and esters. For example,

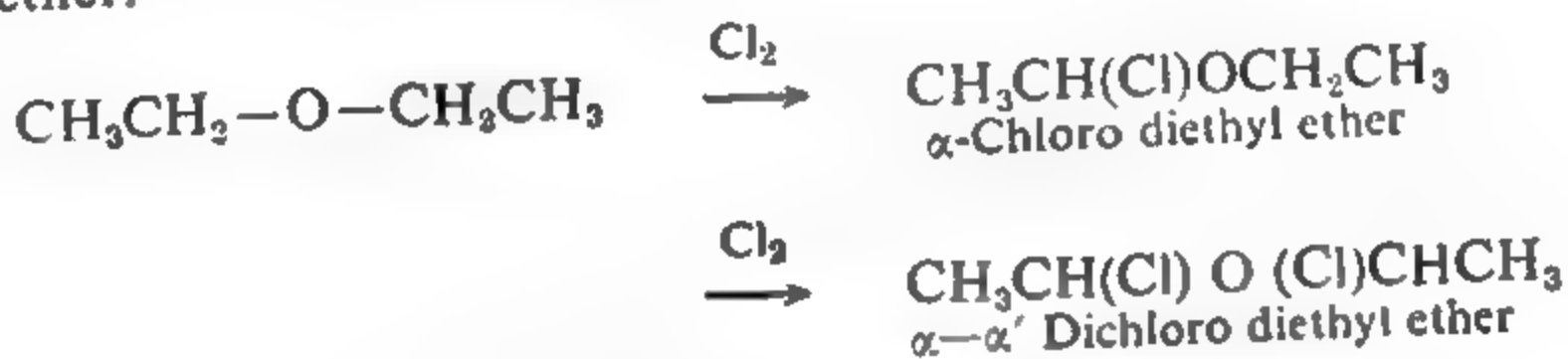


Similarly, with acid anhydrides, ethers are split up to form esters.

For example,



7. **Halogenation.** When treated with chlorine or bromine, under suitable conditions, ethers undergo substitution, forming halogenated products, the α -hydrogen being replaced most readily. For example, diethyl ether reacts with chlorine in the dark to yield α - α' dichloro-diethyl ether.



In the presence of light, all the hydrogens are replaced.



8. **Reduction.** It has been recently shown that ethers, when treated with sodium in liquid ammonia, is reduced to ethane and ethyl alcohol.



9. **Reaction with carbon monoxide.** Ether gives ester when treated with carbon monoxide at $125-180^\circ$ under a pressure of 500 atmospheres, in the presence of boron trifluoride and a little water.



ETHYL ETHER OR ETHER, $\text{C}_2\text{H}_5\text{—O—C}_2\text{H}_5$

The most important member of the series is ethyl ether, and is commonly named as "ether".

Preparation. (1) Ether is prepared in the laboratory as well as on a commercial scale by heating a mixture of ethyl alcohol and concentrated sulphuric acid at 140° . The reaction is known to take place in two stages :



The ethyl hydrogen sulphate formed in the first stage reacts with more of the alcohol giving ether and regenerating sulphuric acid. The latter attacks a further quantity of alcohol producing more of ether as shown above. The process is thus continuous and is often referred to as **Williamson's continuous etherification process**. It is obvious that theoretically only a small amount of sulphuric acid will etherify an unlimited quantity of alcohol, but practically it is not so. The reaction comes to a standstill after some time unless fresh sulphuric acid is added. This is because of the fact that the acid is gradually destroyed on account of its reduction to sulphur dioxide by alcohol and also gets diluted with water evolved during the first stage.

Details of Laboratory Preparation. The apparatus employed for the laboratory preparation of ether consists of a 500 c.c. distillation flask fitted with a dropping funnel and a thermometer. The side tube of the flask is attached to a long water condenser, the lower end of which is fitted into a filtration flask which acts as a receiver (Fig. 1). The side tube of the receiver carries a long rubber tubing, the

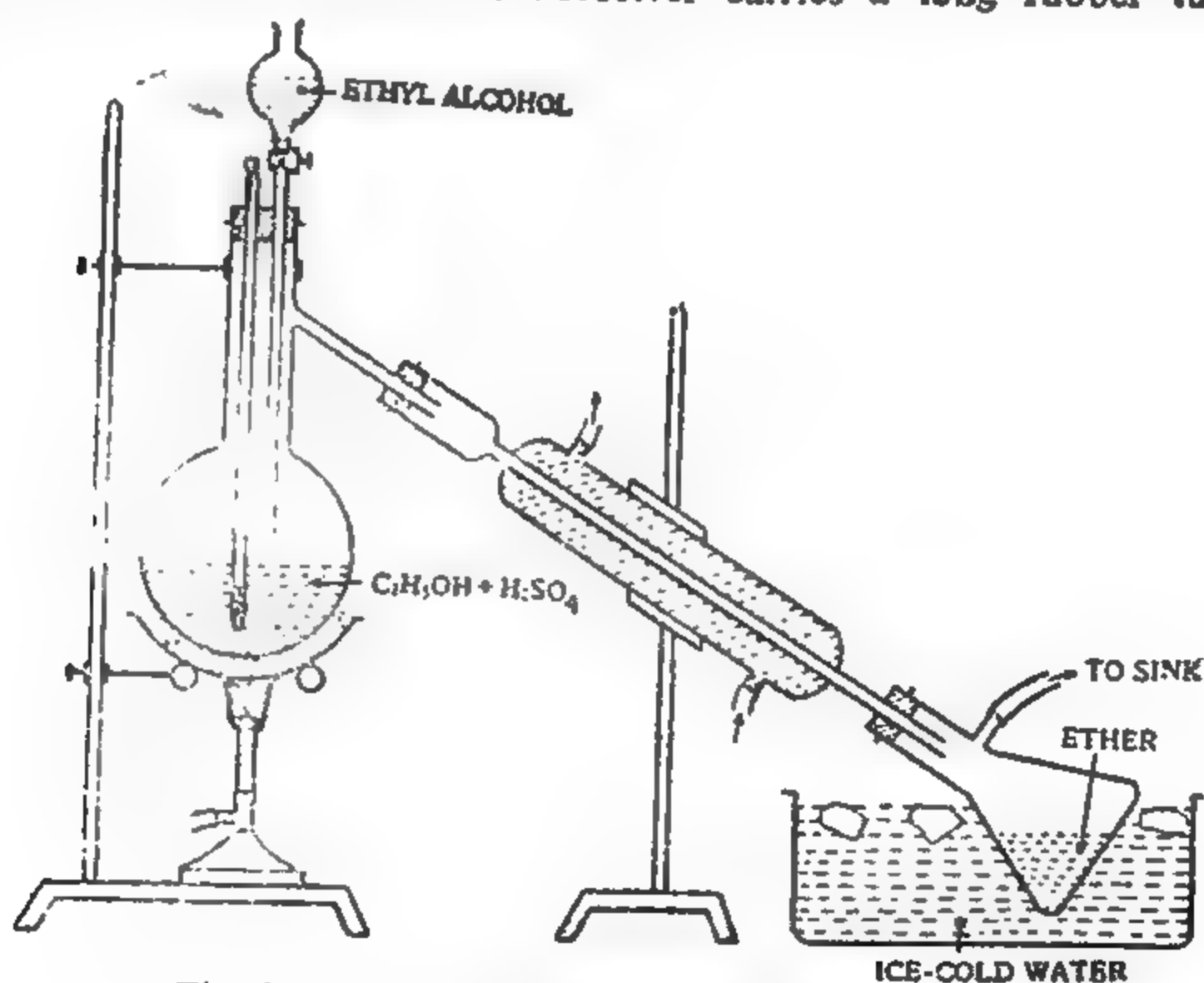


Fig. 1. Laboratory preparation of ether

open end of which is placed in the sink. This is done to keep the vapour of ether away from the burner. The entire apparatus is made leak-proof.

100 ml. of alcohol is taken in the distillation flask and 50 ml. of concentrated sulphuric acid added to it gradually with shaking and cooling. The flask is then heated on a sand bath till the temperature rises to about 140° , when ether begins to distil over. Alcohol is now run in from the dropping funnel at about the same rate at which the distillation occurs and the temperature is maintained at 140° .

The distillate contains ether, mixed with impurities like alcohol, water, carbon dioxide and sulphur dioxide. Ether is purified by shaking first with a dilute solution of sodium hydroxide. The ethereal layer is washed with water and dehydrated by letting it stand over anhydrous calcium chloride for some time. It is then redistilled by heating on a water bath or better on an electric bath when pure ether distils over at $34-35^{\circ}$.

Details of Commercial Preparation. The plant used for the manufacture of ether is diagrammatically shown in Fig. 2. It allows the production of an almost unlimited amount of ether from a single charge of the acid. Pure concentrated sulphuric acid is placed in the ether generator (also known as ether pot) and the required quantity of alcohol added to it. The mixture is then heated by passing superheated steam through a coil immersed in the reaction mixture and the temperature maintained at about 140° . Alcohol is slowly run into the generator from the alcohol feed tank which is placed at a higher level. The vapours issuing from the ether generator consist of ether, alcohol, steam and traces of sulphur dioxide. They first pass up the alkali scrubber down which falls a stream of sodium hydroxide solution which removes the sulphur dioxide. The vapours are then led on to a fractionating column where comparatively high boiling alcohol and water are condensed while the ether vapour escape at the top and are condensed by passing through water condensers. The alcohol-water mixture is taken to another fractionating column for the recovery of alcohol. The alcohol thus obtained is dehydrated and returned to the alcohol-feed tank.

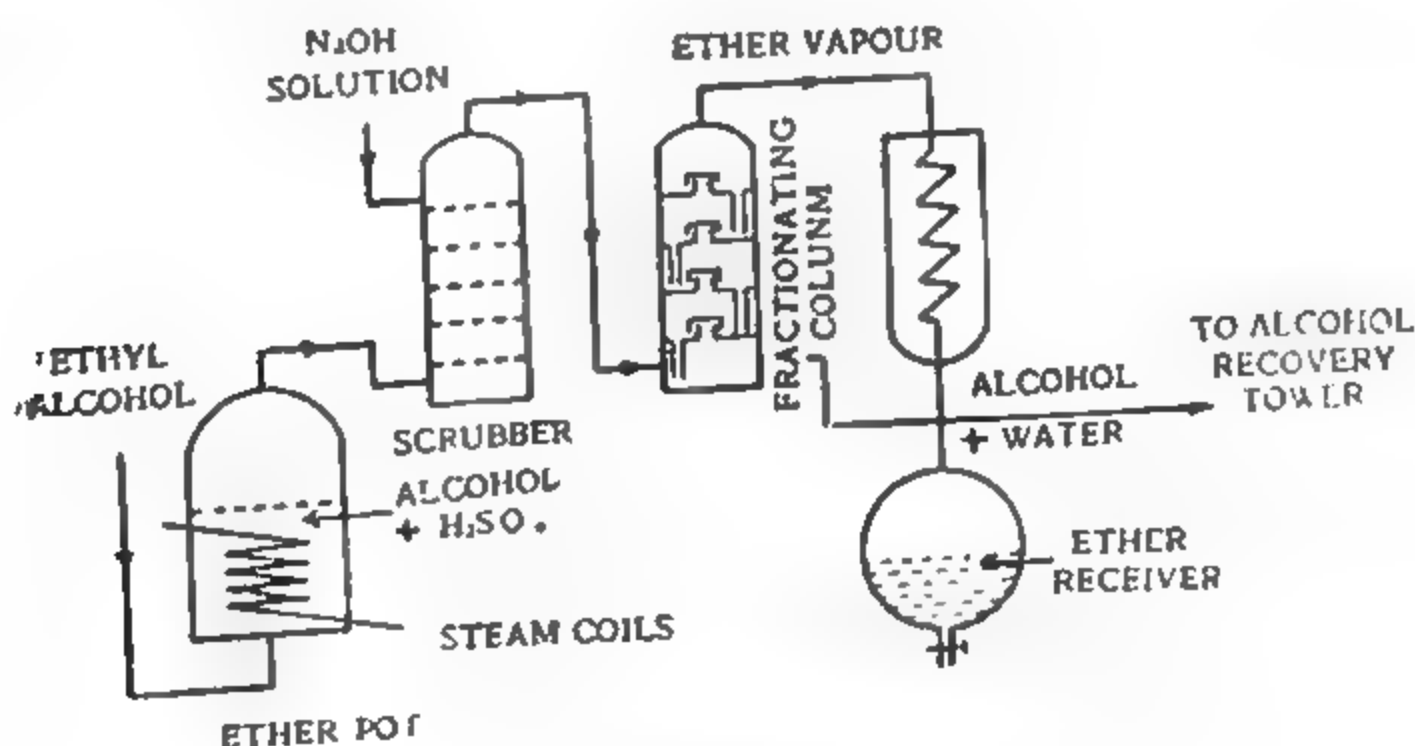


Fig. 2. Manufacture of Ether

The process is continuous, the plant, after being charged with sulphuric acid once, can run for months together.

(2) Ether can also be prepared on a commercial scale by passing ethyl alcohol vapour, under pressure, over heated alumina or aluminium phosphate (see general methods of preparation of ethers).

Properties. Diethyl ether is a colourless, highly volatile liquid boiling at 34°C . It is slightly soluble in water but is completely miscible with alcohol in all proportions.

It is highly inflammable and forms explosive mixture with air—a property which puts ether on a little disadvantage in its use as an industrial solvent.

It gives all the reactions characteristic of ethers.

Uses. (1) Ether is a very valuable *solvent* and is used for extracting organic substances from aqueous solutions. It is employed on a large scale in the manufacture of *collodion* and *artificial silk*.

(2) When rapidly evaporated, ether produces intense cooling and hence it is used as a *refrigerant*. A mixture of ether and dry ice (solid carbon dioxide) is an excellent cooling mixture giving a temperature as low as -110°C .

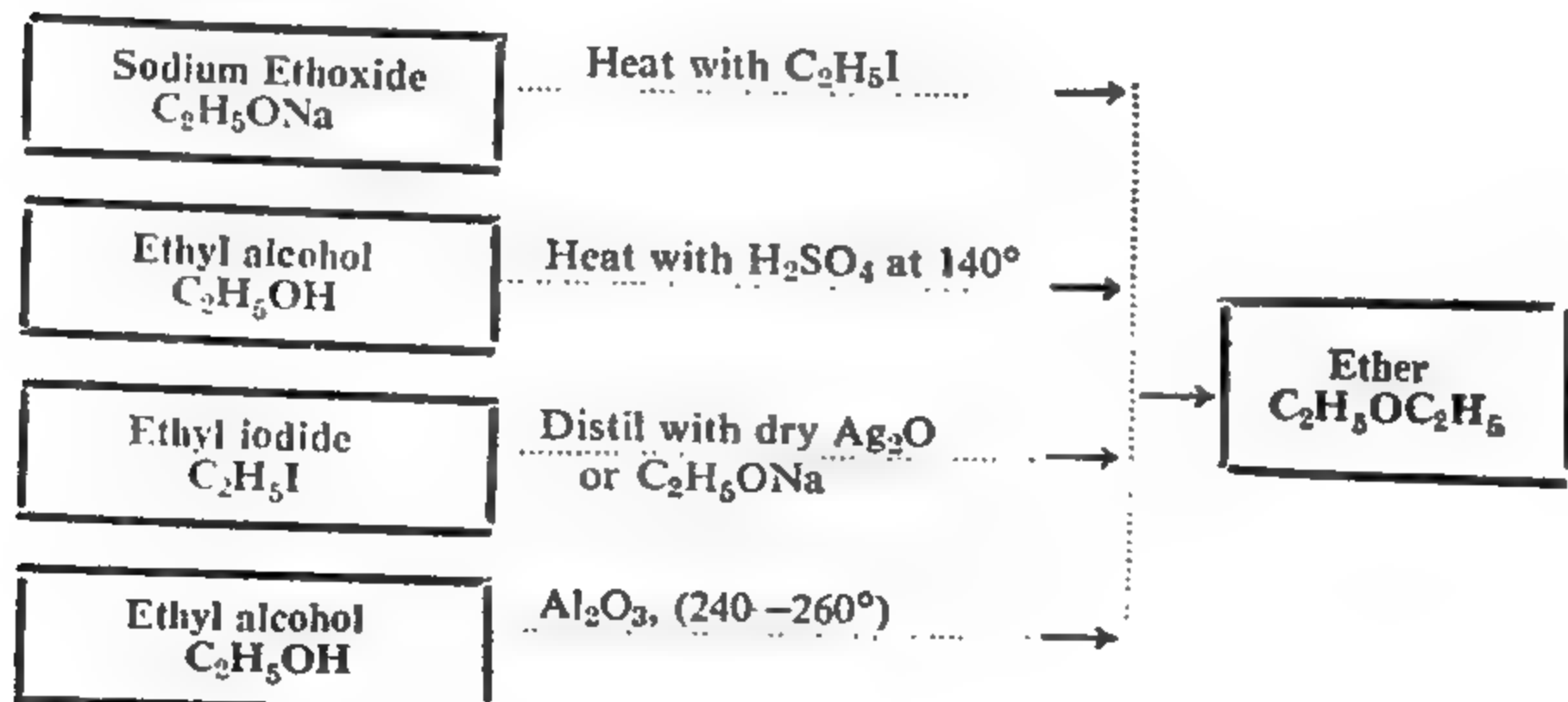
(3) A mixture of alcohol and ether is used as a substitute for petrol, under the name *natalite*.

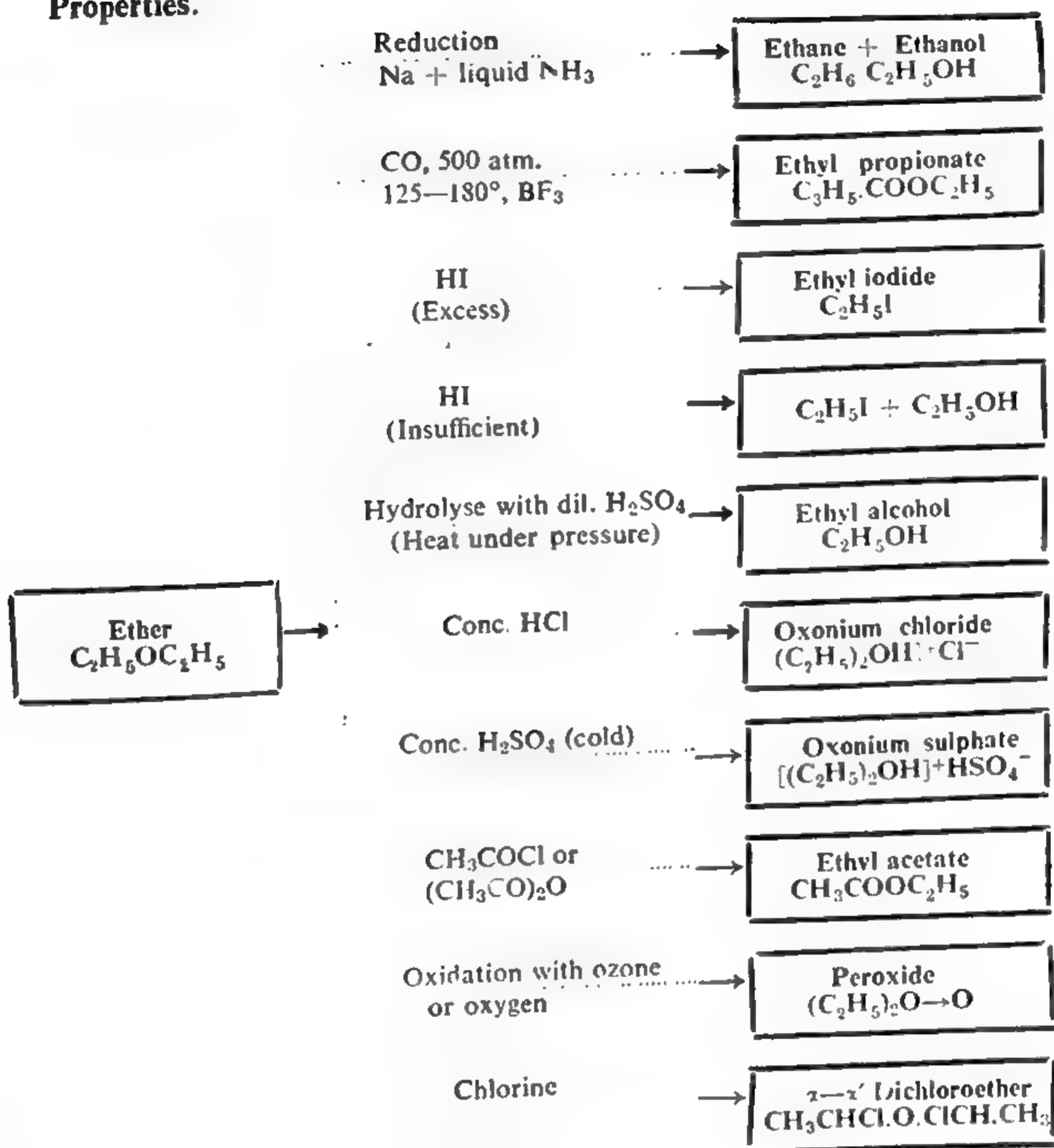
(4) Ether provides an excellent *inert medium* for many organic reactions such as the Wurtz reaction and Grignard reaction.

(5) Ether is most frequently used as an *anaesthetic* in surgery. It is superior to chloroform because it produces unconsciousness without interfering much with the functions of heart and lungs.

SUMMARY OF TYPICAL MEMBER

Preparation.



Properties.**QUESTIONS**

1. Describe the general methods of preparation, properties and uses of aliphatic ethers.

2. Describe briefly the general methods for the preparation of ethers. How do they react with (i) dilute mineral acids (ii) concentrated hydriodic acid (iii) acetyl chloride or acetic anhydride (iv) phosphorus pentachloride?

Mention the important uses of ethers.

3. How is diethyl ether prepared (i) in the laboratory (ii) on a commercial scale?

Discuss the action of the following on ether :

(i) Hydriodic acid (ii) Bromine (iii) Phosphorus pentachloride (iv) Sulphuric acid.

QUESTIONS .

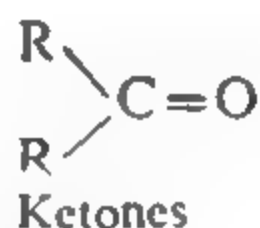
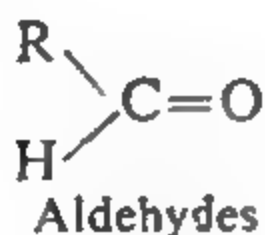
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4. Describe the preparation of diethyl ether from ethyl alcohol. Compare and contrast the properties of ethyl ether and ethyl alcohol.
5. Give four general methods of preparation of ether and four chemical properties of ethyl ether naming the products formed in the latter case. (*Panjab Inter 1961*)
6. How may ethyl ether be prepared in the laboratory? What are its properties and chief uses? What impurities are likely to be present in it? (*Panjab Inter 1956*)
7. Suggest two different schemes by which ether can be obtained from ethanol. Prove analytically and synthetically that ether is the anhydride of ethanol. What is the action of PCl_5 on ethyl ether? (*Panjab Inter 1951*)
8. How will you distinguish chemically ethyl alcohol from diethyl ether? (*Panjab Inter 1951*)
9. Give an account of the physical and chemical properties of ordinary ether. How may it be synthesised from its elements? (*Panjab Inter 1947*)

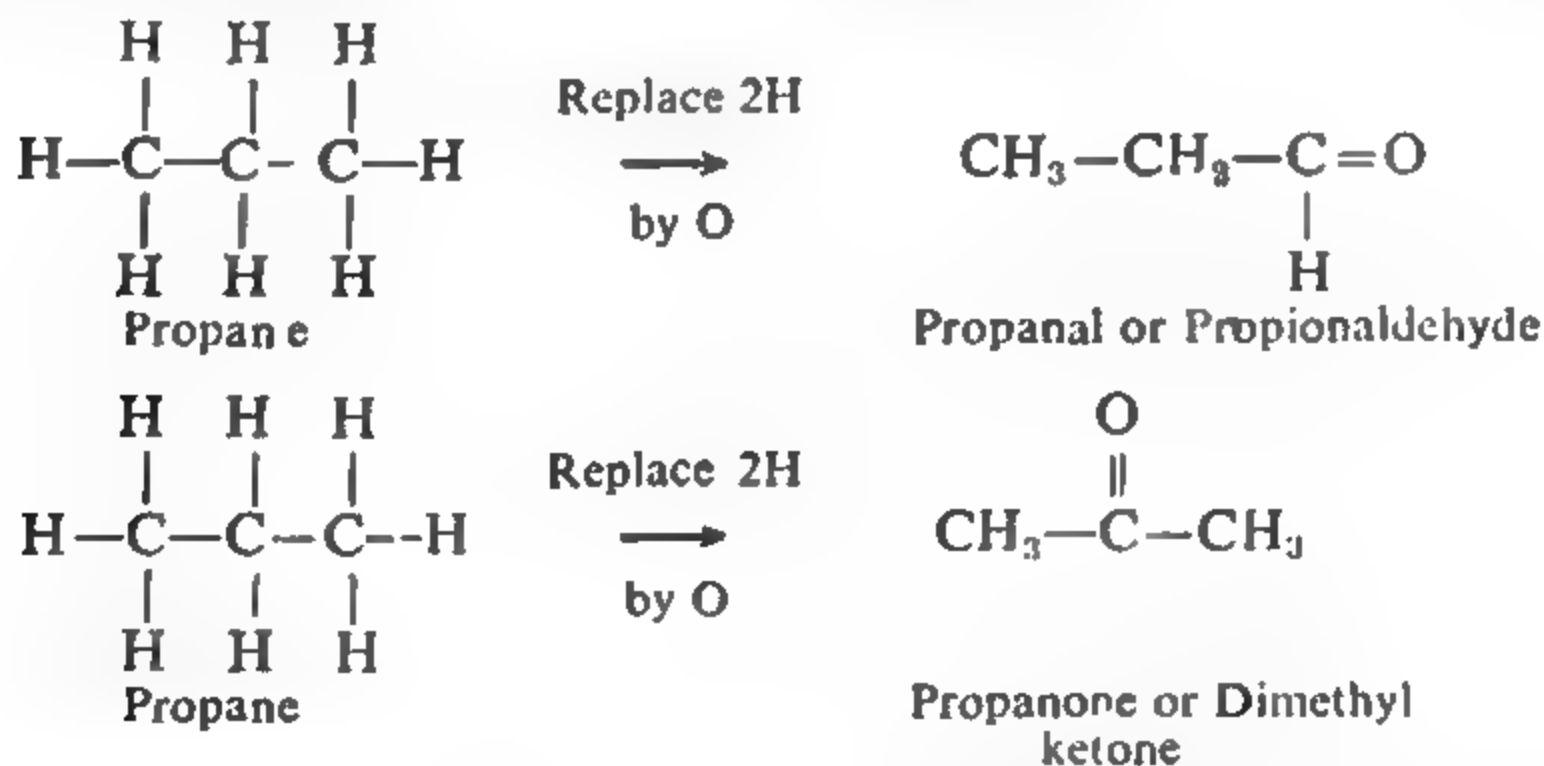
CHAPTER XXXIV

ALDEHYDES AND KETONES

Aldehydes and ketones form two series of compounds isomeric with each other, having the general formula $C_nH_{2n}O$. Both types of compounds contain the bivalent carbonyl group ($>CO$) in their structures. In case of aldehydes, the carbonyl group is united to an alkyl radical and hydrogen atom, while in ketones, it carries two alkyl radicals.



Aldehydes and ketones may be regarded as derived from paraffins by the replacement of two hydrogen atoms linked to a carbon atom, at the end of the chain (in case of aldehydes) and in the middle of the chain (in case of ketones), by a bivalent oxygen atom.



Primary alcohols on oxidation give aldehydes which on further oxidation yield acids: ($RCH_2OH \longrightarrow RCHO \longrightarrow RCOOH$). Hence, aldehydes are also referred to as the *first oxidation products of primary alcohols*. In fact, the name aldehyde originated from *alcohol dehydrogenatum*, meaning alcohol deprived of hydrogen.

Similarly, secondary alcohols on oxidation give ketones which on further oxidation yield acids.



Hence, ketones are called the *first oxidation product of secondary alcohols*.

First few members of the series of both aldehydes and ketones are given below :

Aldehydes

Formula	Common name	I.U.C. name
H.CHO	Formaldehyde	Methanal
CH ₃ .CHO	Acetaldehyde	Ethanal
C ₂ H ₅ .CHO	Propionaldehyde	Propanal
C ₃ H ₇ .CHO	Butyraldehyde	Butanal
C ₄ H ₉ .CHO	Valeraldehyde	Pentanal

Ketones

Formula	Common name	I.U.C. name
CH ₃ .CO.CH ₃	Dimethyl ketone	Propanone
CH ₃ .CO.C ₂ H ₅	Methyl ethyl ketone	Butanone
C ₂ H ₅ .CO.C ₂ H ₅	Diethyl ketone	Pentanone—3
C ₂ H ₅ CO.C ₂ H ₇	Ethyl propyl ketone	Hexanone—3

When both the alkyl radicals are the same, the ketones are said to be *simple* and when the two alkyl radicals are different, they are referred to as *mixed* ketones.

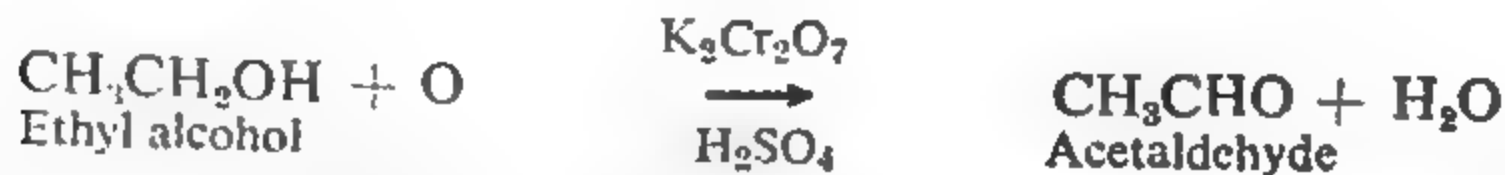
General Methods of Preparation of Aldehydes and ketones. Aldehydes and ketones may be prepared by the following methods :

1. **By oxidation of alcohols.**

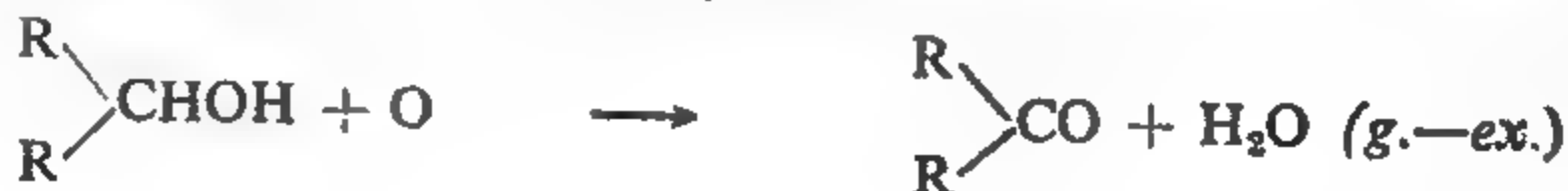
Aldehydes are obtained by the oxidation of primary alcohols with *potassium dichromate and dilute sulphuric acid or chromic anhydride dissolved in glacial acetic acid* or by passing the *alcohol vapour mixed with air over heated silver at 250°* which acts as a catalyst.



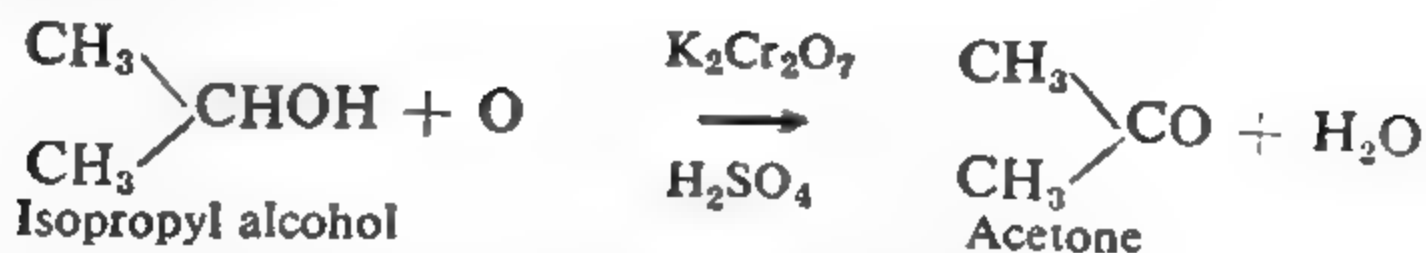
For example,



Ketones are obtained by the oxidation of *secondary* alcohols using the same oxidising agents as for aldehydes.



For example,



2. By catalytic dehydrogenation of alcohols.

Aldehydes can be obtained by passing vapour of *primary* alcohols over finely divided copper at 300° .



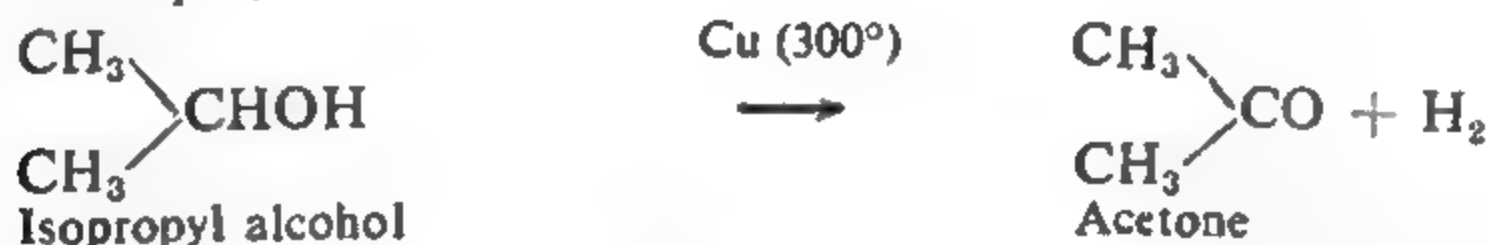
For example,



Ketones are produced by using *secondary* alcohols.

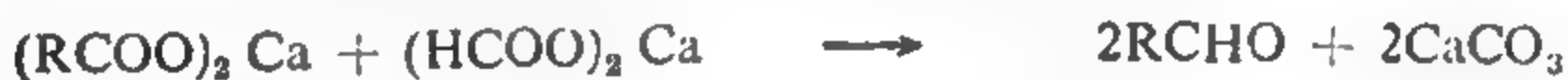


For example,



3. By distillation of calcium (or barium) salts of fatty acids.

Aldehydes are produced by heating a mixture of calcium (or barium) salts of formic acid and of any other fatty acid.



For example,



Ketones are obtained by heating calcium (or barium) salts of any fatty acid (other than formic acid).



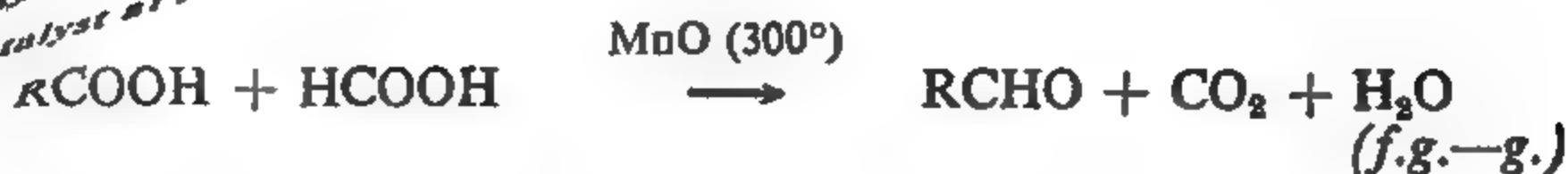
For example,



4. By catalytic decomposition of acids.

Aldehydes can also be obtained by passing a mixture of the vapours of formic acid and other higher fatty acid over manganous oxide as

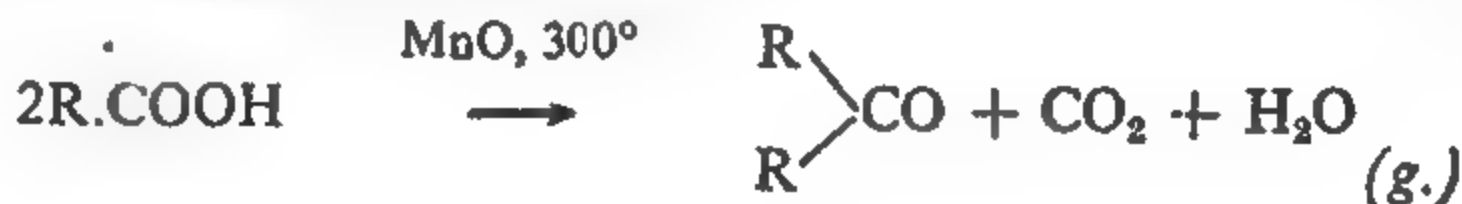
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catalyst at 300°.



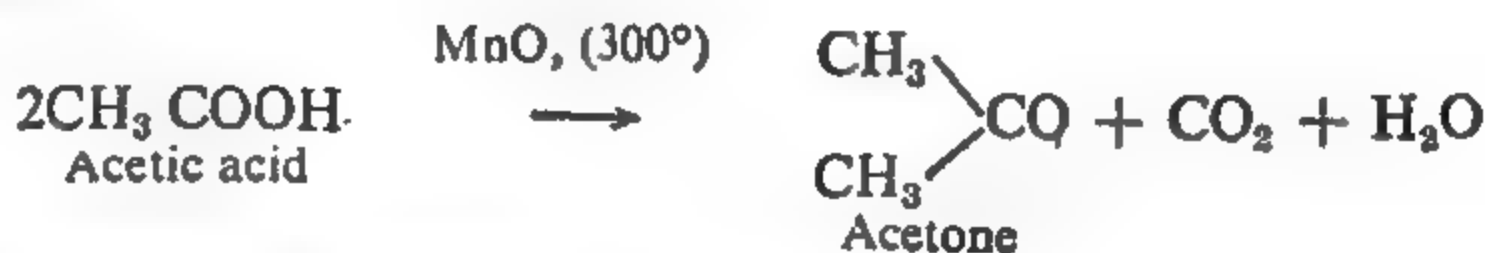
For example,



Ketones are produced by passing the vapour of any fatty acid, other than formic acid, over MnO at 300°.

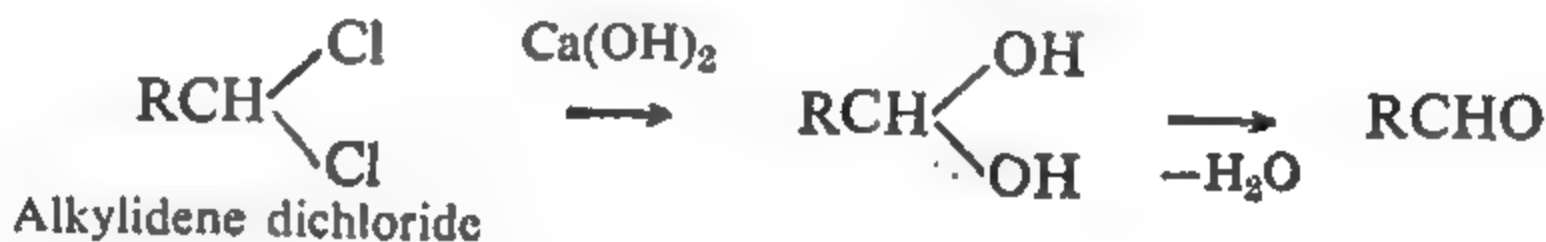


For example,

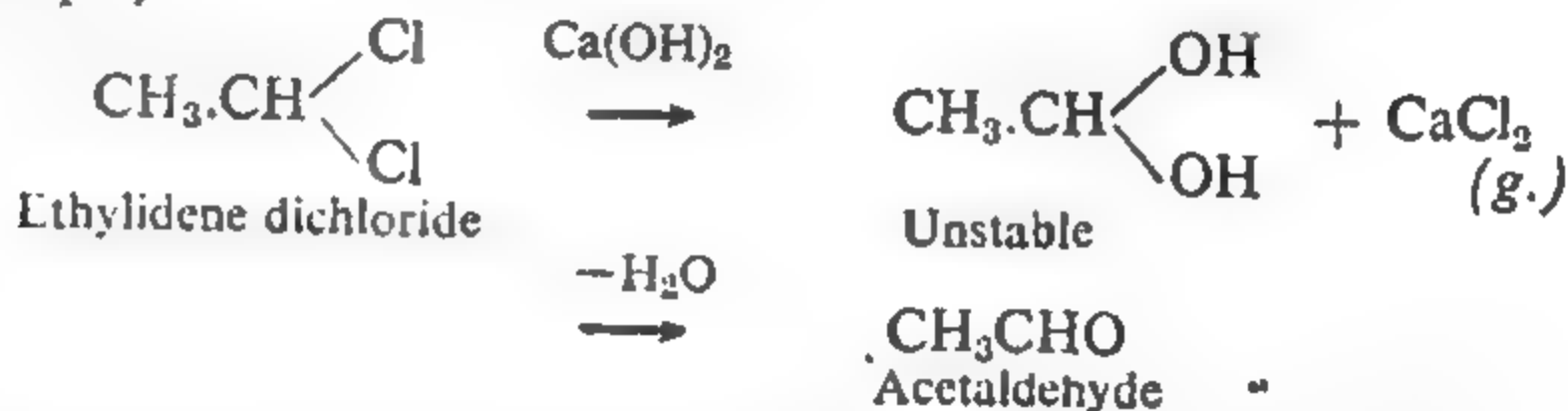


5. By the hydrolysis of dihalides.

Aldehydes are produced by the hydrolysis of alkylidene dihalides (in which the two halogen atoms are attached to a *terminal* carbon atom) with *mild* alkalies.

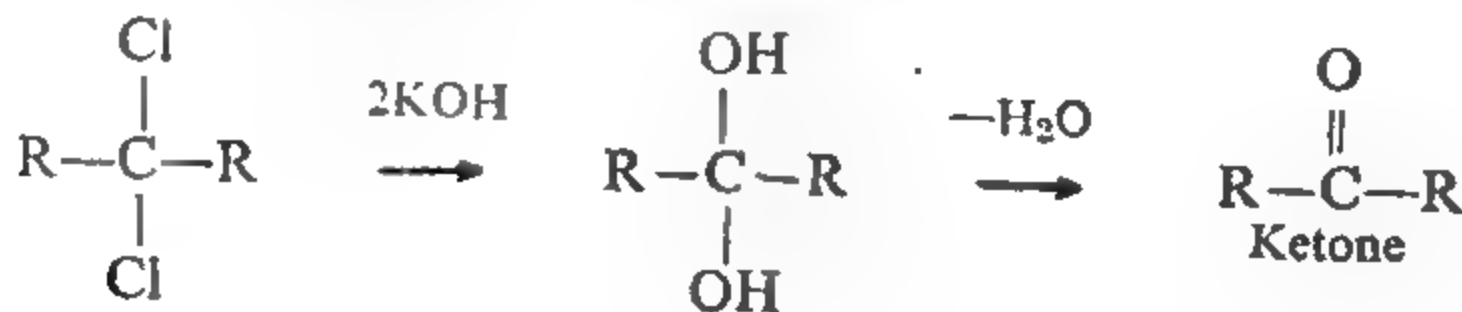


For example,

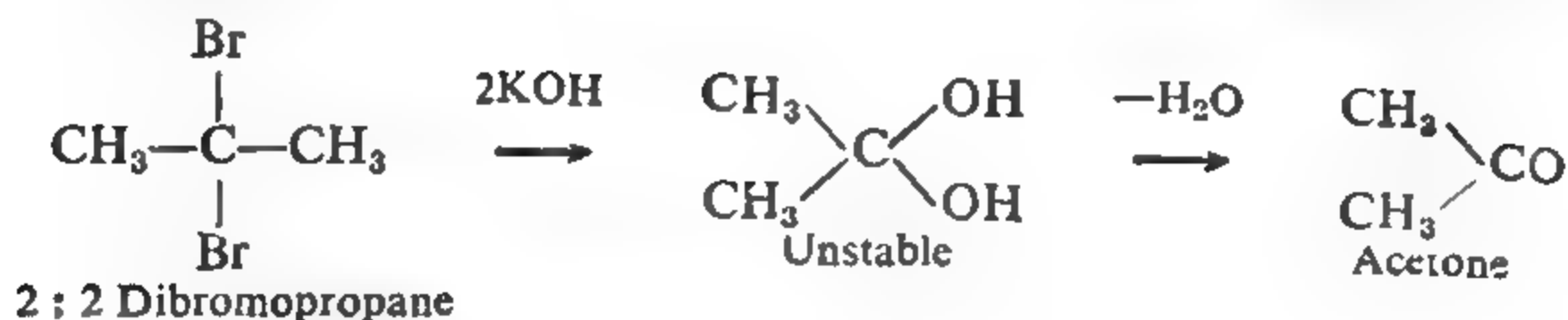


Since aldehydes get resinified with strong alkalies, the above hydrolysis is carried out by boiling with a mild alkali such as baryta or an aqueous suspension of calcium oxide.

Ketones are formed by the hydrolysis of alkylidene dihalides (in which the two halogen atoms are attached to a carbon atom other than a terminal one) with alkali.



For example,

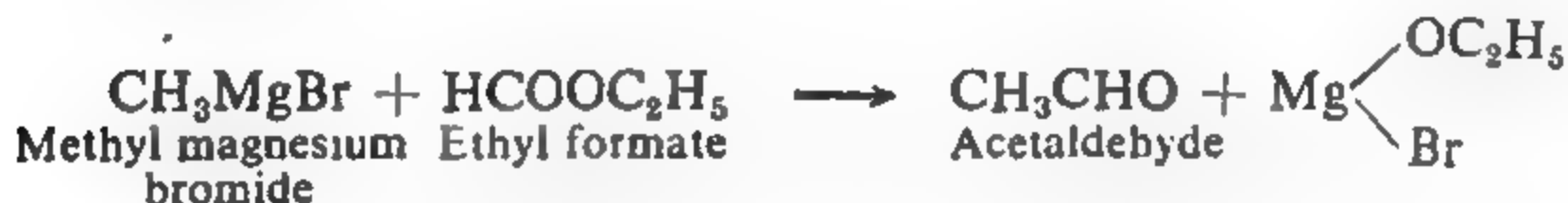


6. From Grignard reagents.

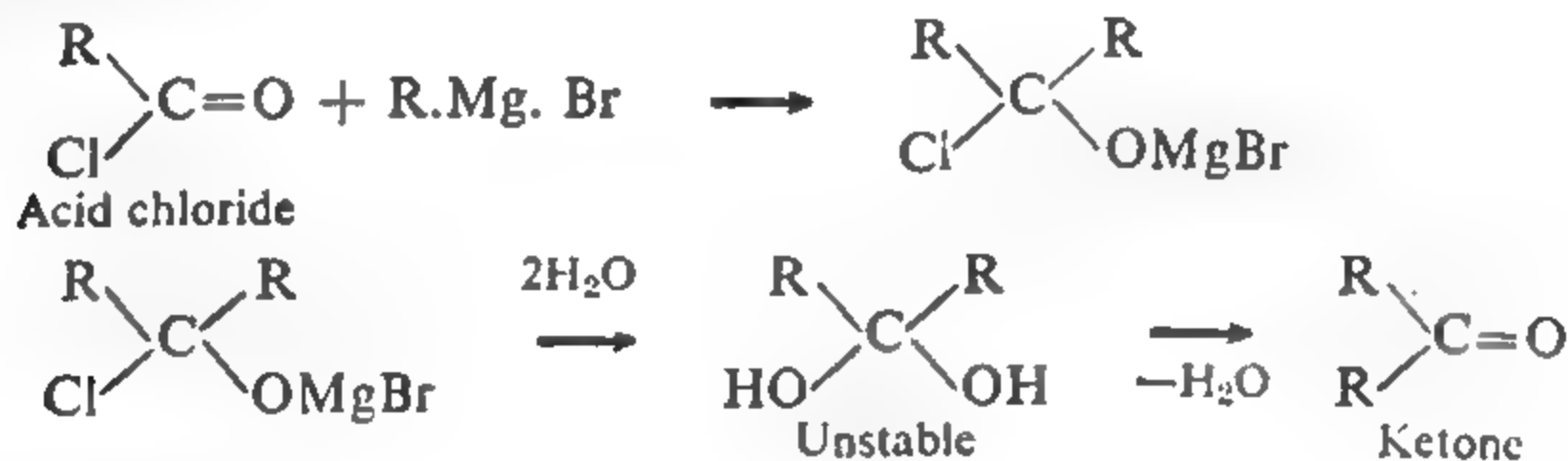
Aldehydes can be prepared by the action of Grignard reagents with excess of *ethyl formate*.



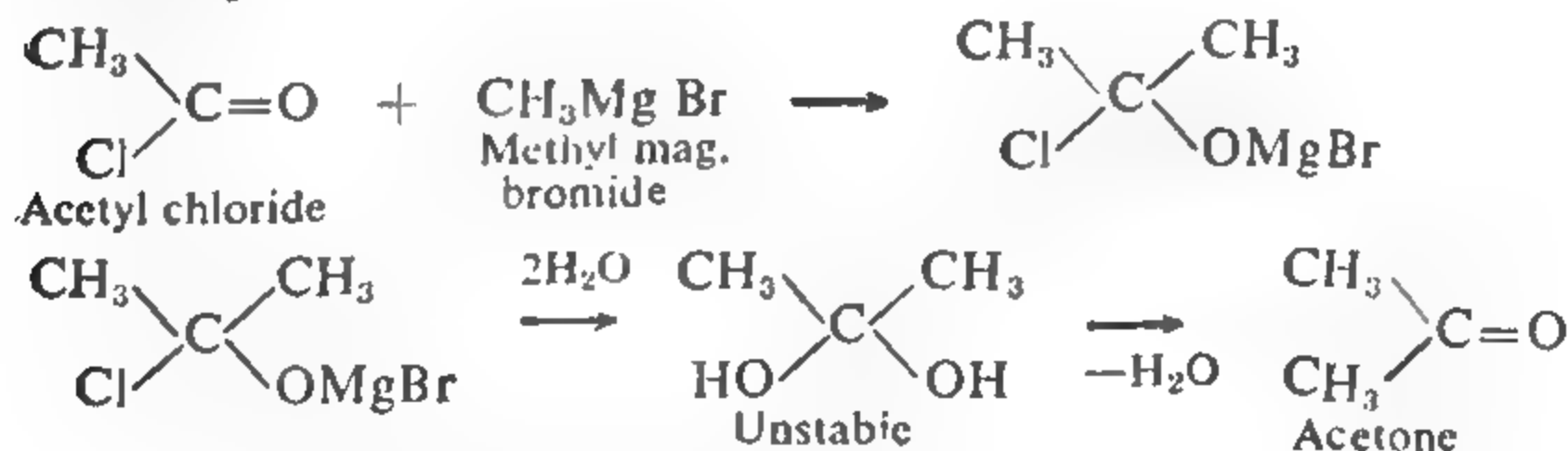
For example,



Ketones can be prepared by the action of *acid chlorides* with Grignard reagents.

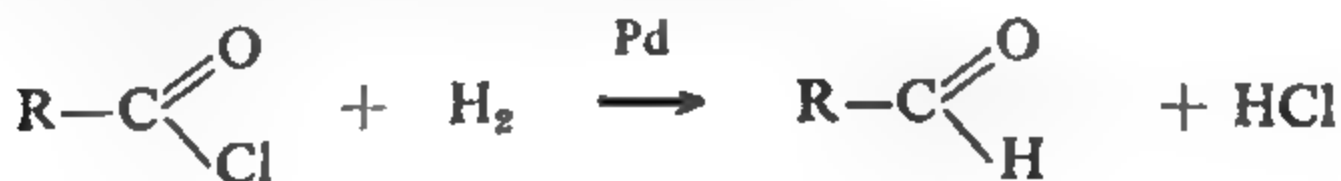


For example,



7. By the reduction of acid chlorides.

Aldehydes can be prepared by the reduction of acid chlorides with hydrogen in the presence of palladium catalyst precipitated on barium sulphate (which acts as a poison and checks the reduction of aldehyde to alcohol). (*Rosenmund's reduction*).



For example,



Ketones. There is no analogous method for the preparation of ketones.

Physical Properties. Formaldehyde, the first member of the aldehyde series, is a gas at ordinary temperatures. All other aldehydes and ketones up to about C_{11} are colourless, mobile liquids, the higher members are solids. As a rule, aldehydes possess an unpleasant pungent odour while ketones have a pleasant smell. Even in the case of aldehydes, the higher members possess a fruity odour so much so that aldehydes containing 8 to 15 carbon atoms are used in perfumery.

The first few members of both aldehyde and ketone series are freely miscible with water but solubility rapidly falls with the rising molecular weights, the higher members being particularly insoluble in water. They are, however, freely soluble in organic solvents such as ether, alcohol, etc.

Chemical Properties.

I. REACTIONS COMMON TO ALDEHYDES AND KETONES

A. Common Reactions due to Carbonyl Group.

Because of the presence of the common $>\text{C}=\text{O}$ group in their structure, aldehydes and ketones exhibit a number of common properties which are known as the reactions of the carbonyl group.

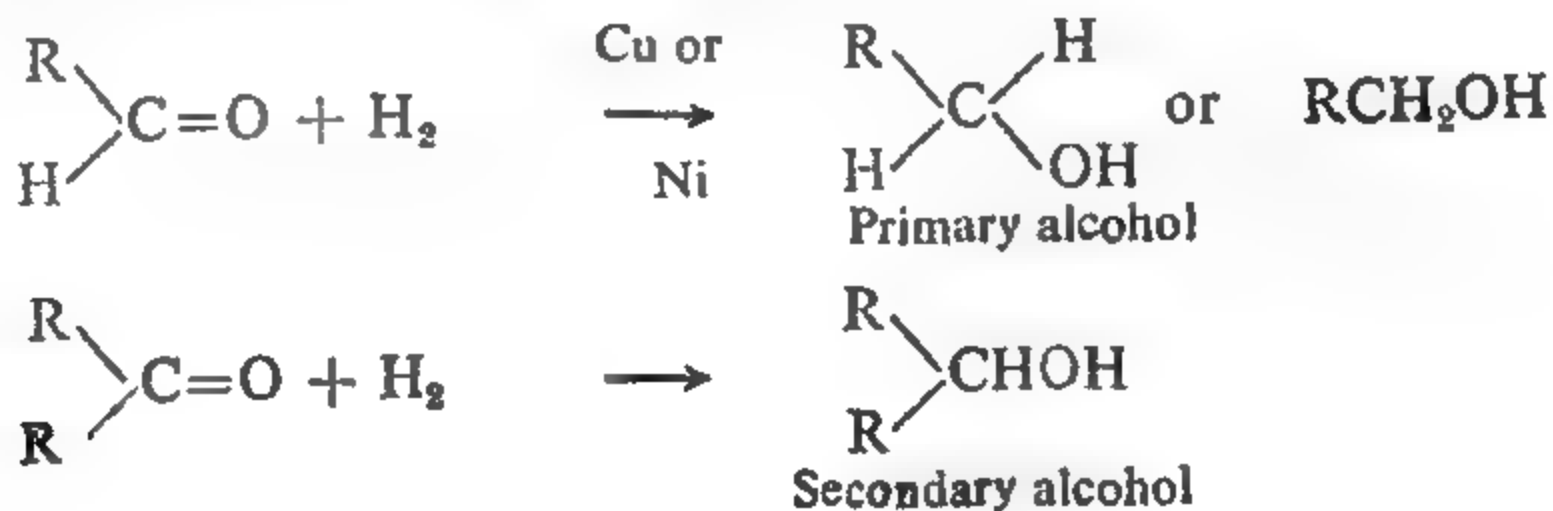
These reactions are of two types :

(i) *Addition reactions involving addition at the double bond of the carbonyl group.*

(ii) *Replacement reactions involving replacement of the oxygen of the carbonyl group by other atoms or groups.*

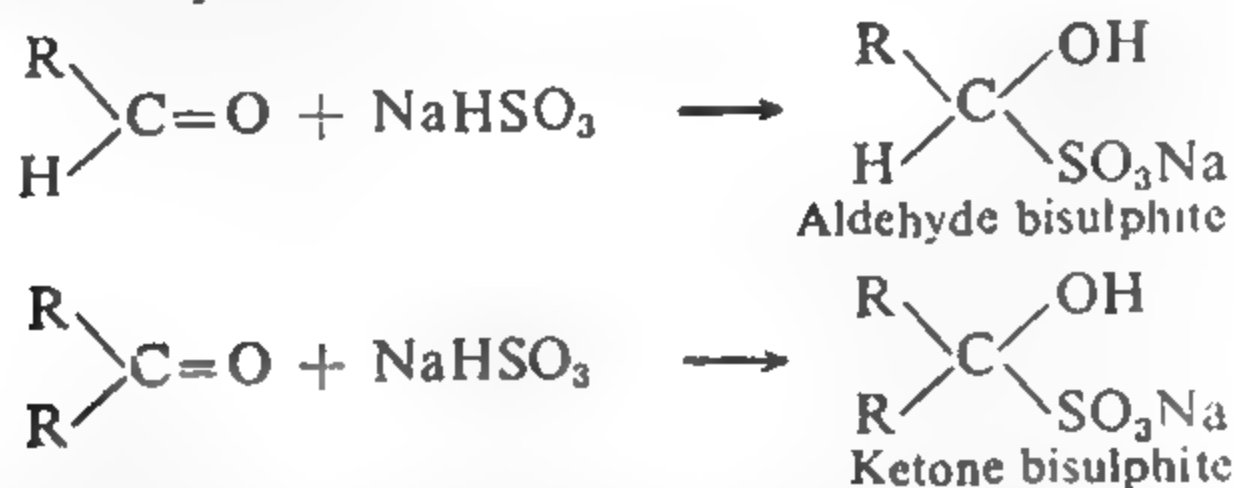
(a) Addition Reactions of the Carbonyl Group.

(1) **Addition of hydrogen.** Both aldehydes and ketones add a molecule of hydrogen in the presence of a catalyst (copper or nickel) forming primary and secondary alcohols respectively.



Reduction may also be carried out by nascent hydrogen, prepared by the action of sodium amalgam and water or a metal and dilute acid. Another elegant reducing agent is lithium aluminium hydride.

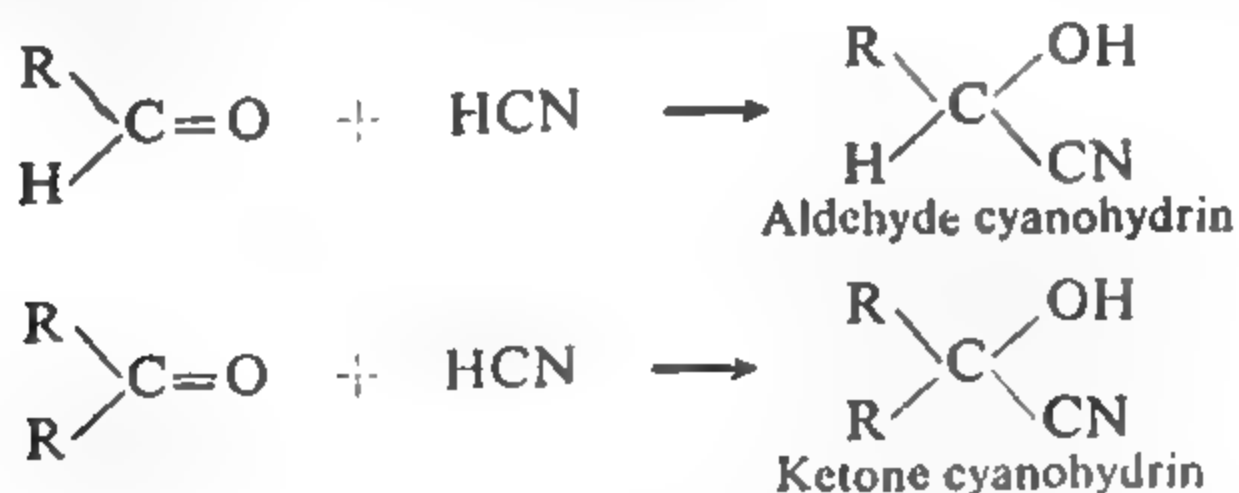
(2) **Addition of sodium bisulphite.** Both aldehydes and ketones react with sodium bisulphite forming crystalline compounds known as *bisulphite compounds*.



These bisulphite compounds are readily soluble in water but are insoluble in a saturated solution of sodium bisulphite. Hence, the reaction is carried out by shaking the aldehyde or ketone with a saturated solution of sodium bisulphite when the bisulphite compound of aldehyde or ketone is thrown out.

On warming with dilute acids or alkalis, the bisulphite compounds are decomposed to give back the original aldehyde or ketone. Hence, the formation of these compounds is used for the *purification* and *separation* of aldehydes and ketones.

(3) **Addition of hydrogen cyanide.** Both aldehydes and ketones add on hydrogen cyanide to form *cyanohydrins*. The reaction is carried out by treating the carbonyl compound with sodium cyanide and dilute sulphuric acid.

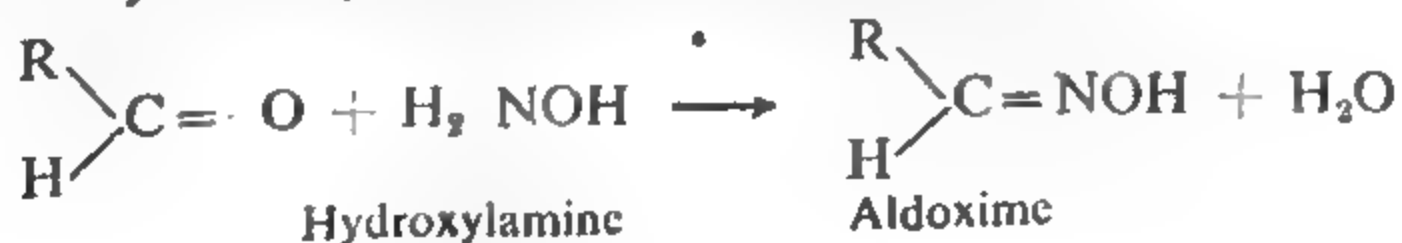


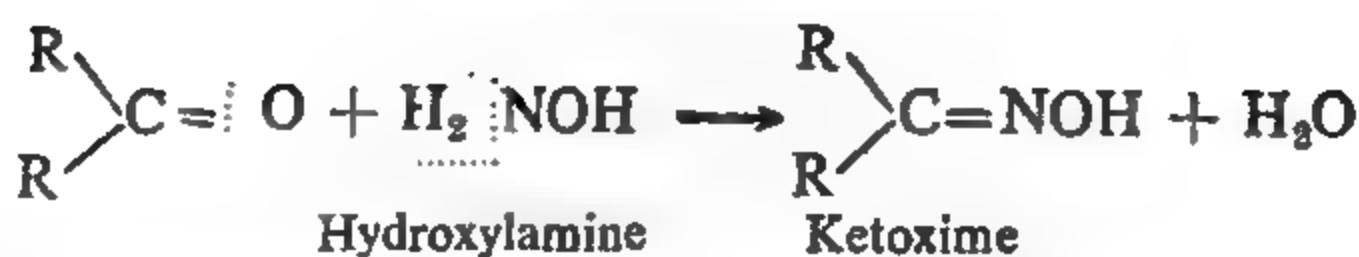
(b) Replacement Reactions of the Carbonyl Group.

Both aldehydes and ketones react with many reagents to form products in which the oxygen of the carbonyl group is replaced by a bivalent group or two monovalent atoms. These reactions generally involve the elimination of a molecule of water.

The important replacement reactions are given below :

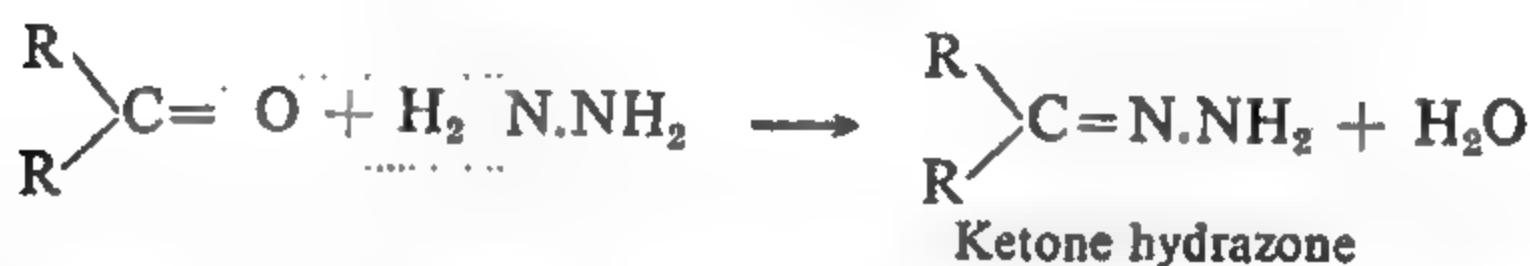
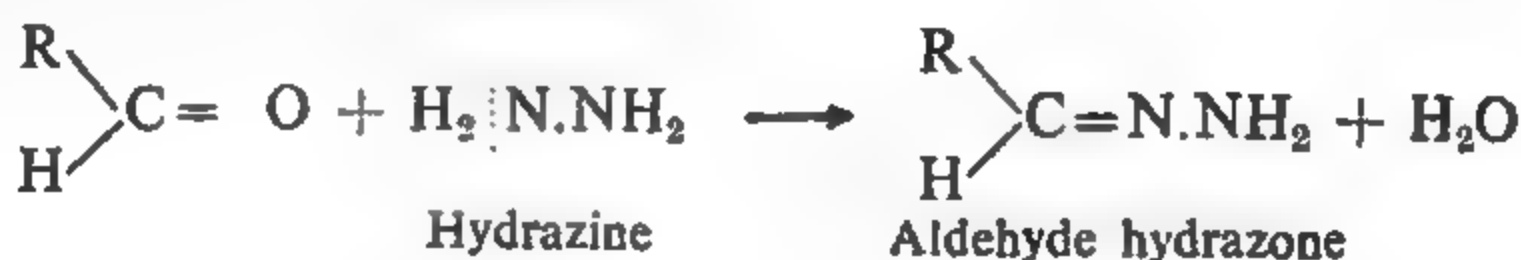
(1) **Reaction with hydroxylamine.** Both aldehydes and ketones react readily with hydroxylamine forming *oximes*.



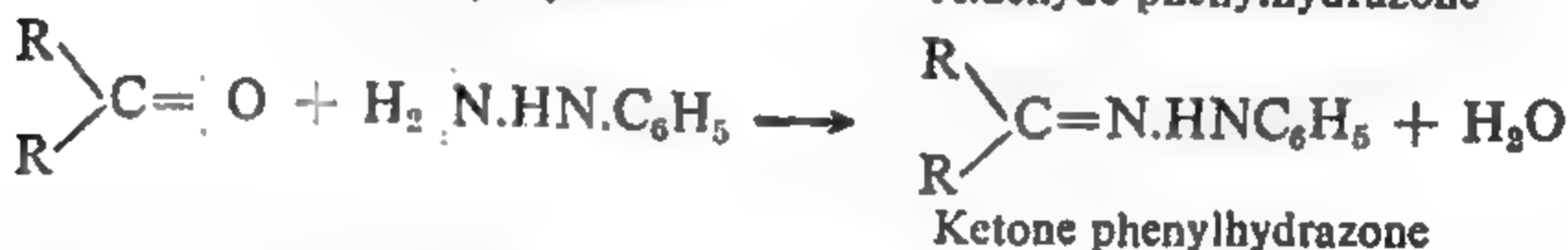
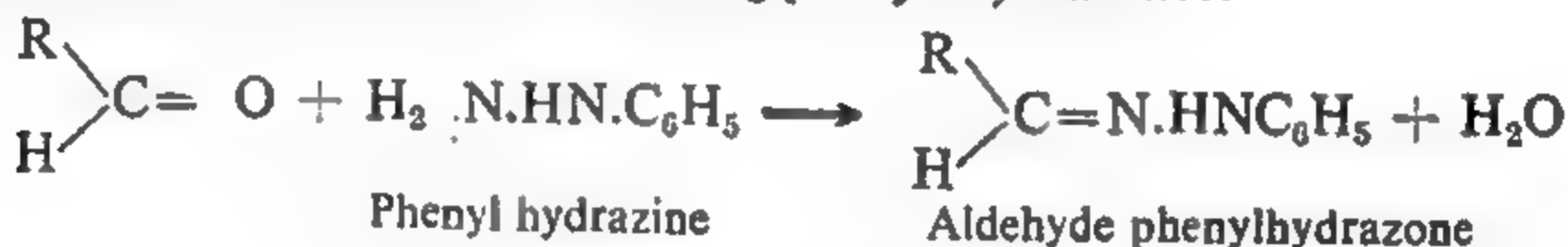


Oximes are well-defined crystalline solids and may be used to identify carbonyl compounds.

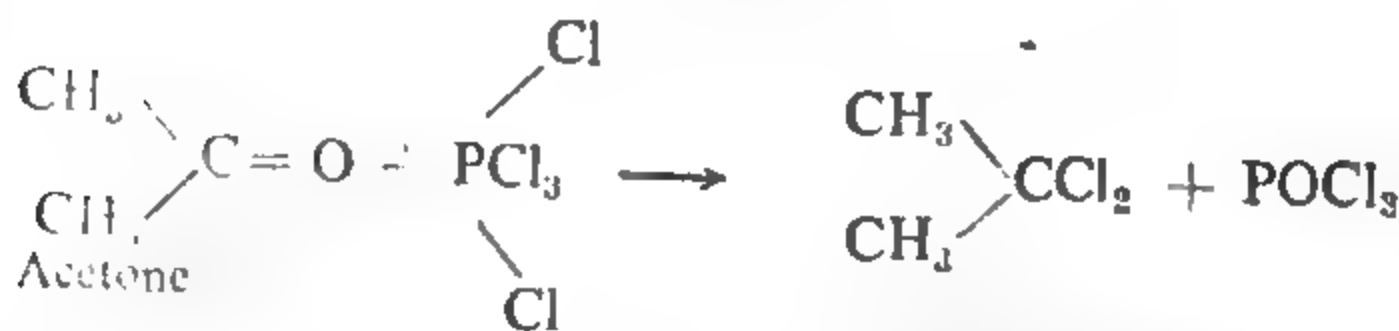
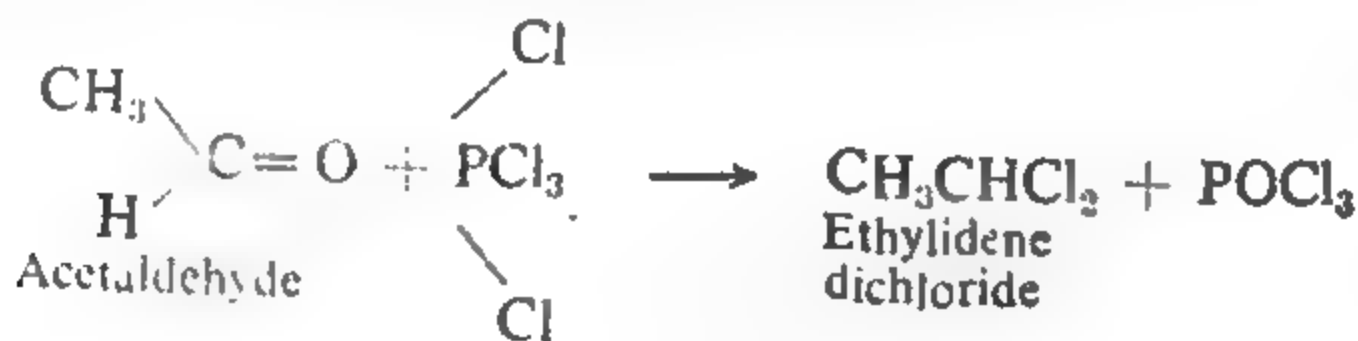
(2) **Reaction with hydrazine.** Both aldehydes and ketones react with hydrazine to form *hydrazones*.



(3) **Reaction with phenyl hydrazine.** Both aldehydes and ketones react with phenyl hydrazine forming *phenyl hydrazones*.



(4) **Reaction with phosphorus pentachloride.** Both aldehydes and ketones react with phosphorus pentachloride when the oxygen of the carbonyl group is replaced by two chlorine atoms.

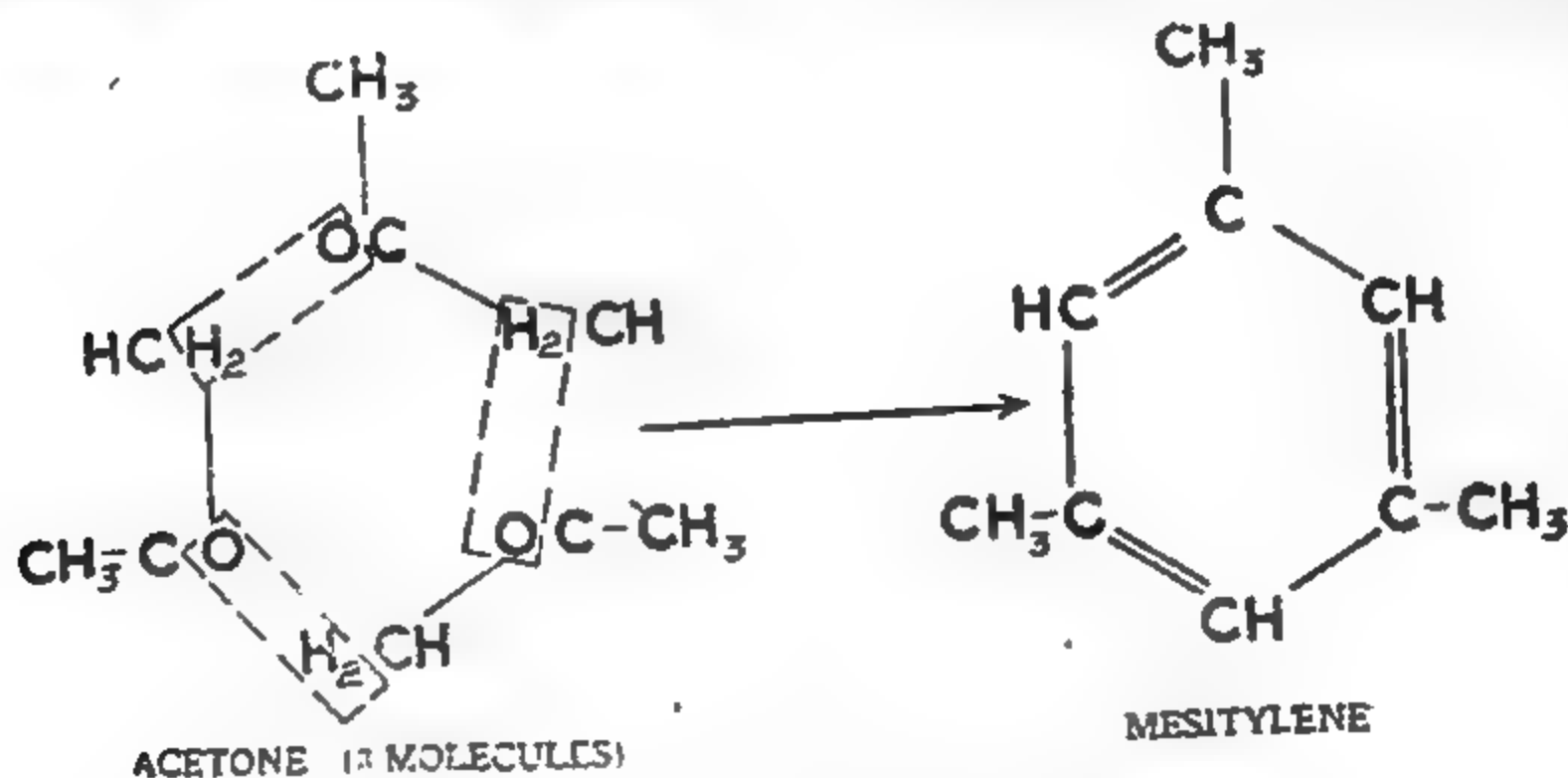


2 : 2 Dichloropropane

B. Common Reactions due to Alkyl Group

Apart from the carbonyl group, aldehydes and ketones have one thing more in common, *viz.*, the alkyl radical. Hence, both aldehydes and ketones give the following reactions :

Similarly, acetone when distilled with sulphuric acid yields *mesitylene*.

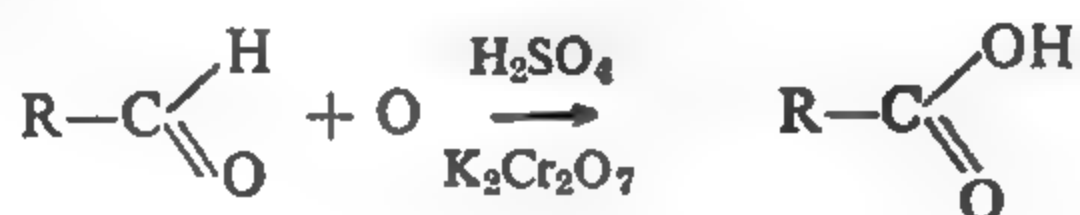


II. REACTIONS GIVEN BY ALDEHYDES ONLY

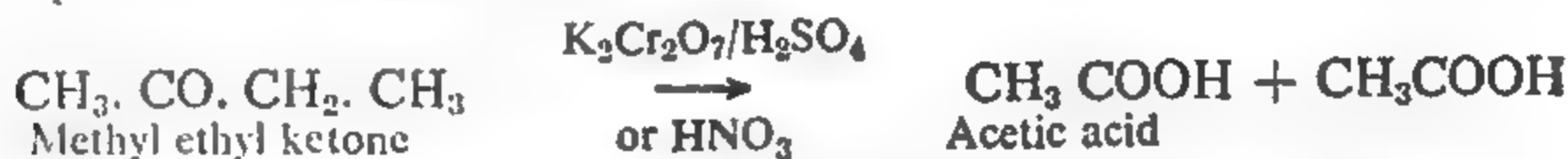
Because of the presence of active hydrogen atom in aldehydes and its absence in ketones, the two families differ considerably from each other. Thus, the following reactions are given only by aldehydes :

(1) **Oxidation.** Aldehydes are readily oxidised to acids containing the same number of carbon atoms.

For example,

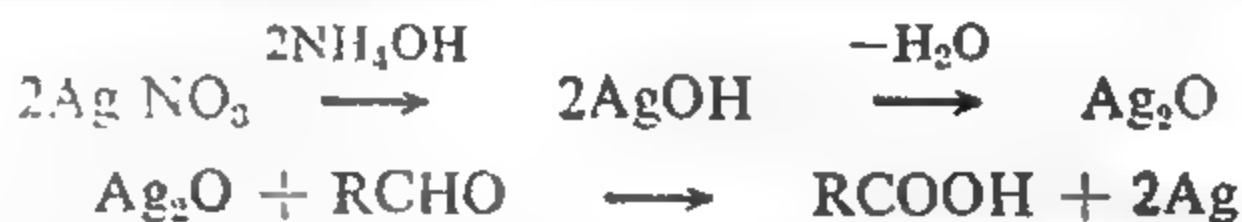


Ketones *cannot* be *easily* oxidised. On more drastic treatment, however, they get oxidised giving acids with lesser number of carbon atoms than present in the original ketone. Oxidation is accompanied by rupture of the molecule, e.g.,



(2) **Reducing properties.** Since aldehydes can be readily oxidised, they act as strong reducing agents.

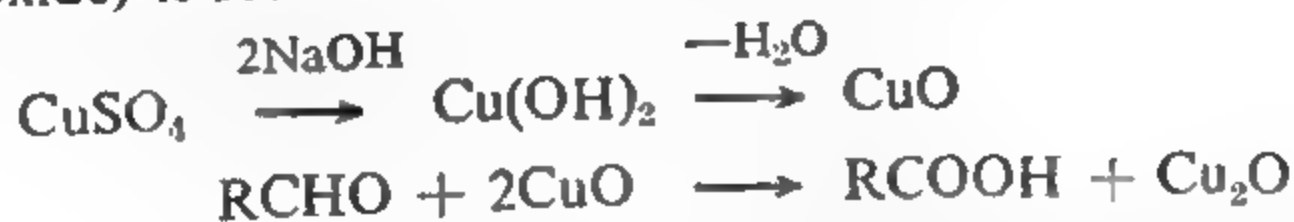
(i) They reduce *ammoniacal solution of silver nitrate* to metallic silver.



The metallic silver forms a mirror on the walls of the containing vessel and serves as a test for aldehydes.

(ii) They also reduce *Fehling solution*, that is, an alkaline solution of copper sulphate (containing Rochelle salt to prevent its precipitation as

hydroxide) is reduced to red cuprous oxide.



This reaction is also used for the *identification* of aldehydes.

Ketones do not reduce Fehling solution or ammoniacal silver nitrate.

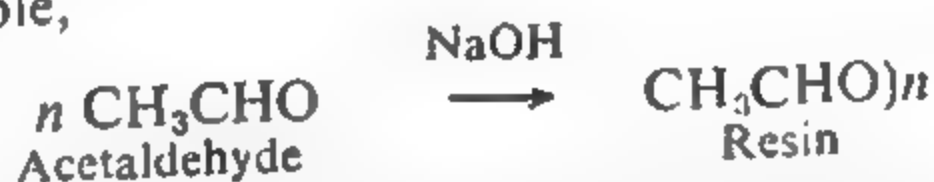
(3) **Schiff's reaction.** When a dilute solution of an aldehyde is added to magenta solution (rosaniline hydrochloride—a red dye), which has been decolorised by sulphur dioxide, the original red colour is restored immediately. This is known as *schiff's reaction* and is used as a *test* for aldehydes.

Ketones do not respond to schiff's reaction. Acetone, however, restores the colour of magenta but *very slowly*.

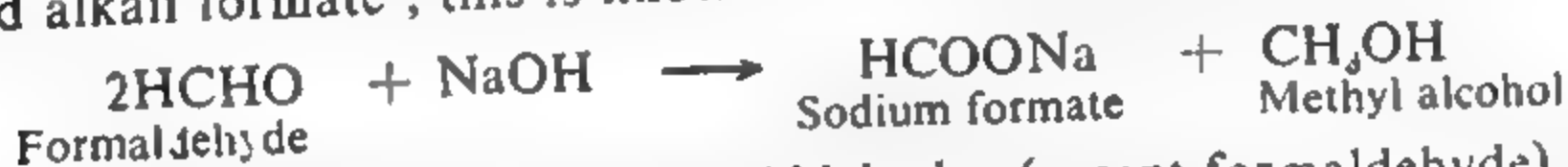
The mechanism of the reaction is not known.

(4) **Resinification.** Aldehydes (except formaldehyde) when warmed with a concentrated alkali solution give dark coloured resinous products known as **aldehyde resins**.

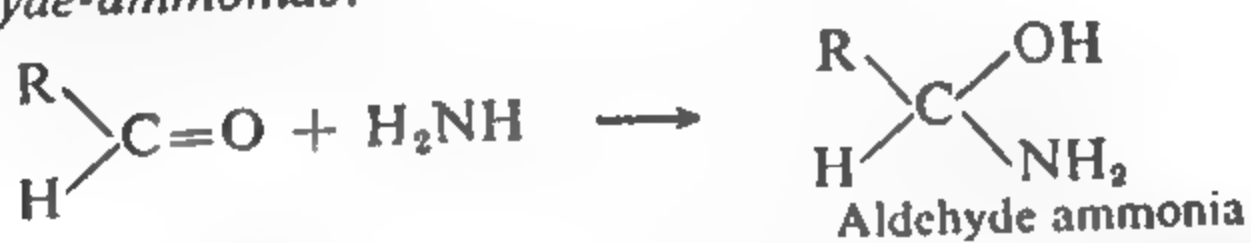
For example,



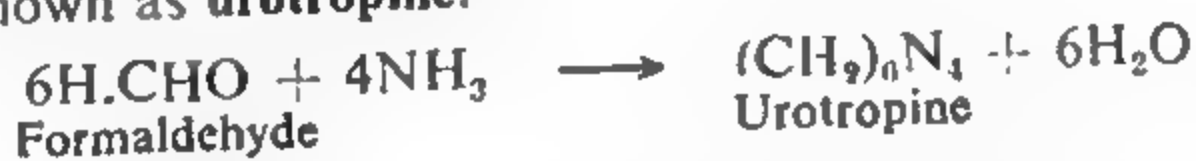
Formaldehyde, on the other hand, gives a mixture of methyl alcohol and alkali formate, this is known as **Cannizzaro's reaction**.



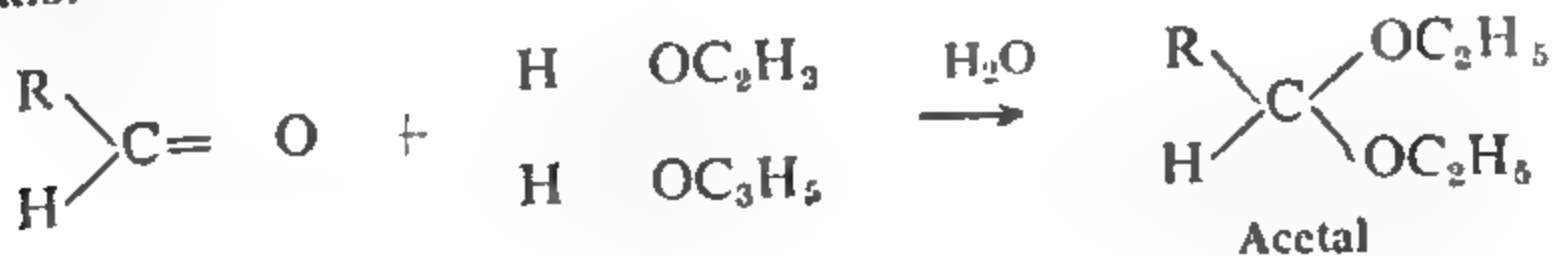
(5) **Reaction with ammonia.** Aldehydes (except formaldehyde) react with ammonia in ethereal solution forming addition products named as *aldehyde-ammonias*.



Formaldehyde, on the other hand, gives hexamethylene tetramine, also known as **urotropine**.



(6) **Reaction with alcohols.** Aldehydes, when warmed with an alcohol in the presence of a little HCl or anhydrous copper sulphate, form **acetals**.



(7) **Reaction with aniline.** Aldehydes react with aniline to form *anils*.



(8) **Polymerisation.** The lower aldehydes readily undergo polymerisation to give a variety of products under different conditions (see individual members).

INDIVIDUAL MEMBERS OF ALDEHYDES

FORMALDEHYDE, METHANAL, H.CHO

1. **Laboratory Preparation.** Formaldehyde is prepared in the laboratory by the catalytic oxidation of methyl alcohol. A platinum spiral or platinised asbestos is used as a catalyst. The apparatus is shown in Fig. 1.

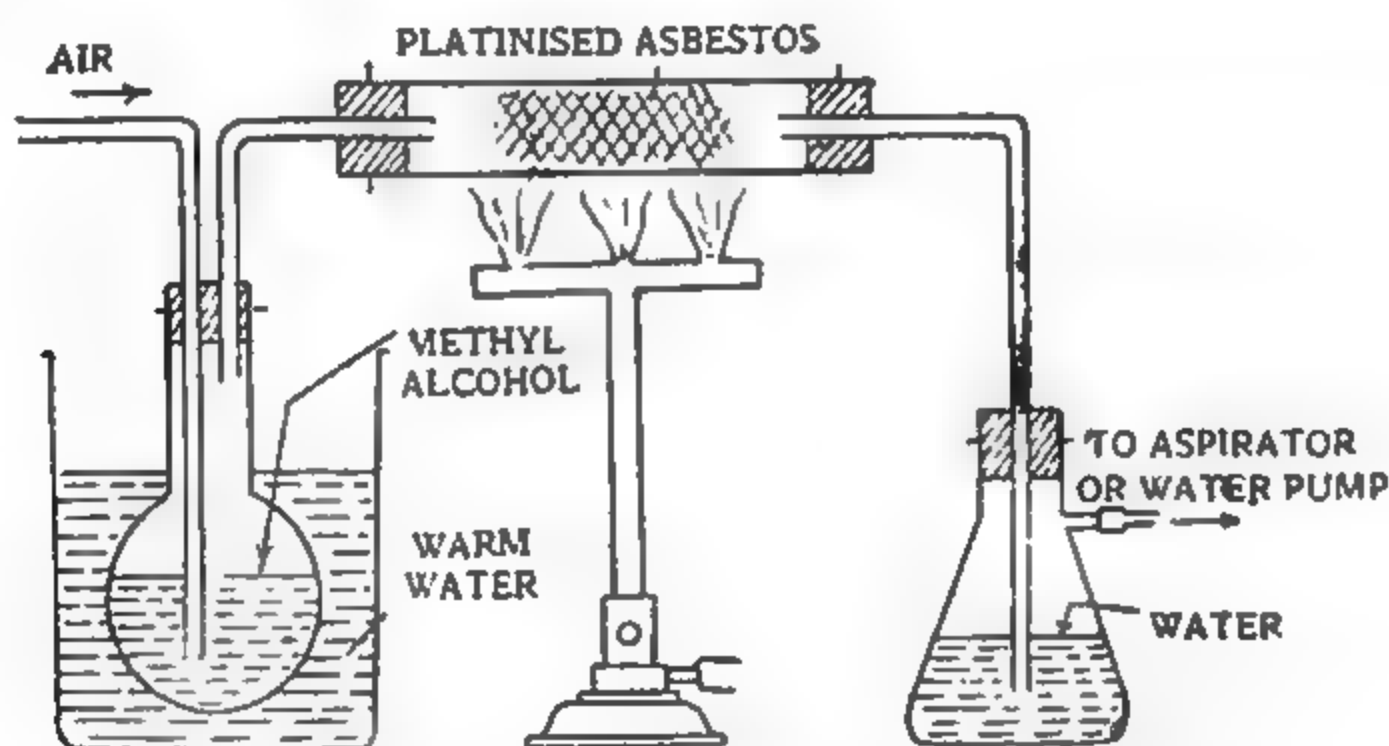


Fig. 1. Preparation of Formaldehyde from Methanol.

Methyl alcohol is taken in a round bottom flask connected to a combustion tube filled with platinised asbestos. The combustion tube is further connected to a filtration flask as shown. A steady current of air is led into methyl alcohol through a glass tube, by applying suction in the filtration flask with the help of a water pump or an aspirator. The flask containing methyl alcohol is placed in a water bath kept at about 40°C. The combustion tube is heated in the meantime. Methyl alcohol vapour carried by air, when passed over heated platinised asbestos, get oxidised to formaldehyde (gas) which is absorbed in water in the filtration flask to give *formalin*. (A 40 per cent aqueous solution of formaldehyde is known as formalin).

2. **Manufacture.** (i) Formaldehyde is prepared industrially also by the catalytic oxidation of methyl alcohol. A mixture of methyl alcohol vapour and air is passed over a catalyst, consisting of molybdenum trioxide and ferric oxide. About 95 per cent of methyl alcohol is oxidised to formaldehyde which is dissolved in water giving formalin.



(ii) Formaldehyde is also prepared on a large scale by the controlled oxidation of methane *under pressure*, in the presence of catalyst such as

molybdenum oxide.



Physical Properties. Formaldehyde is a colourless, pungent smelling gas, readily soluble in water. It can be very easily liquefied, the liquid boiling at -21°C .

Chemical Properties. Formaldehyde responds to many of the general reactions of aldehydes such as additions of hydrogen, hydrogen cyanide, sodium bisulphite; condensation with hydroxyl amine, hydrazine, phenyl hydrazine; oxidation with potassium dichromate, permanganate; reduction of Fehling solution, ammoniacal solution of silver nitrate; Schiff's reaction, etc. But it differs from other aldehydes in certain respects. The difference probably arises from the fact that formaldehyde is structurally different from other aldehydes in having a hydrogen atom linked to the $-\text{CHO}$ group instead of an alkyl radical.

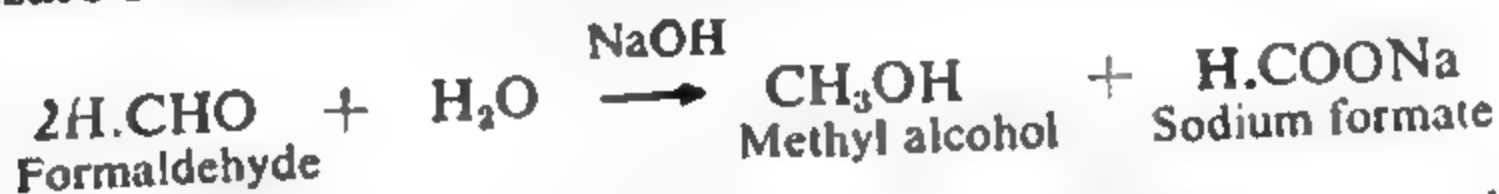
Following are the distinctive reactions of formaldehyde.

(1) **Reaction with ammonia.** When treated with ammonia, it does not form aldehyde-ammonia but gives instead a white crystalline compound, *hexamethylene tetramine* or *urotropine*.



Urotropine or aminoform is used in medicine as a treatment for gout and rheumatism and also as a urinary antiseptic.

(2) **Reaction with aqueous sodium hydroxide.** When treated with a concentrated solution of sodium hydroxide, formaldehyde undergoes **Cannizzaro's reaction** forming methyl alcohol and sodium formate.



(3) **Polymerisation.** Formaldehyde readily undergoes polymerisation yielding different products under different conditions.

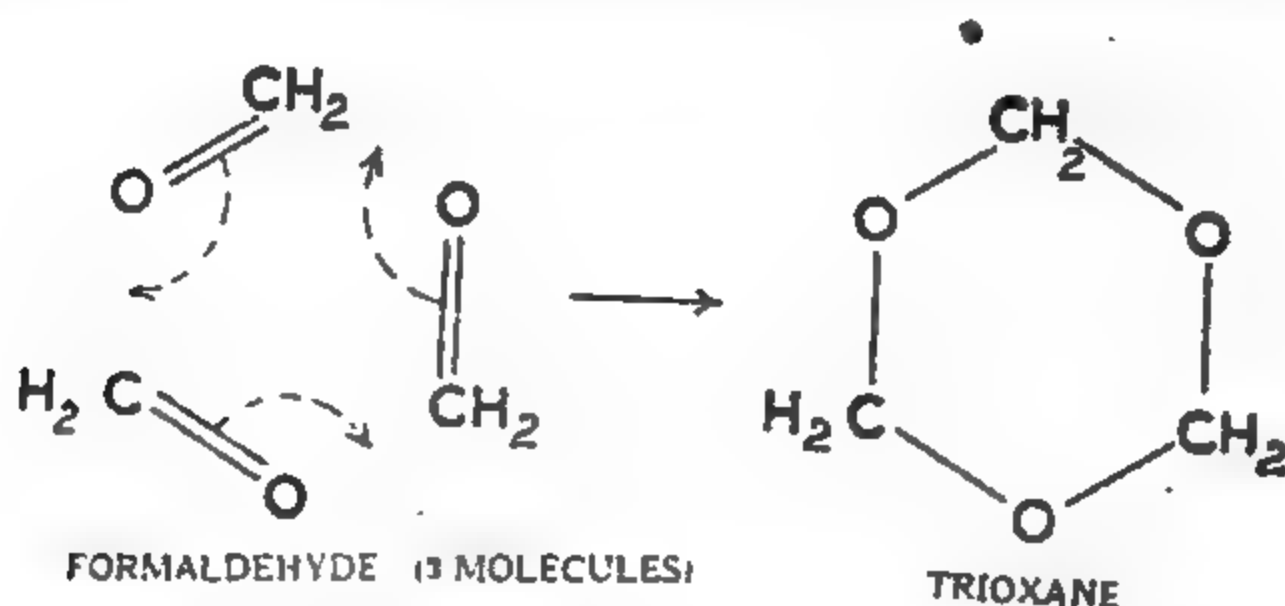
(i) When an aqueous solution of formaldehyde is evaporated to dryness, a white crystalline solid (m.p. $121-123^\circ$) is obtained. This is called **paraformaldehyde** and, in fact, is a mixture of chain polymers of the formula $(\text{CH}_2\text{O})_n \cdot \text{H}_2\text{O}$ where n varies from 6 to 50.



Paraformaldehyde regenerates formaldehyde on heating.

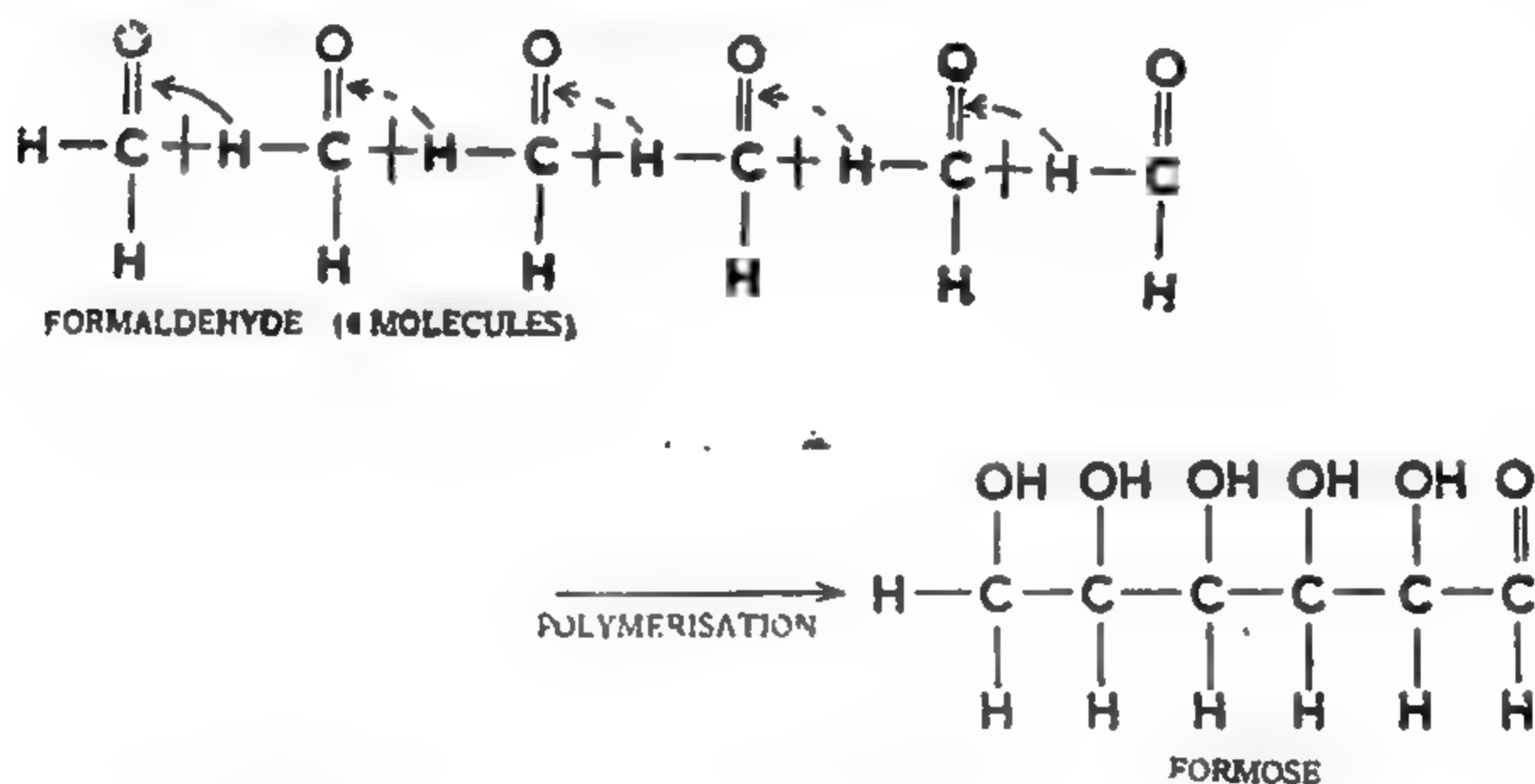
(ii) When distilled from a 60 per cent aqueous solution containing about 2 per cent sulphuric acid, formaldehyde gives **trioxymethylene** or

trioxane. Also when allowed to stand at room temperature, formaldehyde gas slowly undergoes polymerisation giving trioxane.



Trioxane is a white solid (m.p. $61-62^\circ$), soluble in water. On heating it readily yields formaldehyde.

(iii) When treated with weak alkalies, for instance, calcium hydroxide, formaldehyde polymerises to give a mixture of sugars of the formula $C_6H_{12}O_6$, known as **formose**. The sugars are presumably formed through a chain of aldol condensations.



(4) **Condensation with phenol.** Formaldehyde readily condenses with phenol, on heating, giving artificial resins and plastics known as **bakelite**. These are extensively used in the preparation of telephone parts, electric switches, etc.

Uses. Formaldehyde is placed in the market in the form of a 40 per cent aqueous solution known as *formalin*. It is used as a *disinfectant* for sterilising surgical instruments; as a *preservative* for biological specimens; for the production of *bakelite* and other *plastics* and also as a *reducing agent* in the silvering of mirrors.

Tests. Formaldehyde can be identified by the usual reactions of aldehydes.

It also gives the following specific tests, not given by any other aldehyde :

(i) A freshly prepared solution of pyrogallol is mixed with formaldehyde solution and excess of concentrated hydrochloric acid added to it. After the lapse of a few minutes, a white precipitate is obtained which rapidly turns pink and finally deep red.

(ii) To an aqueous solution of formaldehyde are added 2-3 drops of phenyl hydrazine, 1-2 drops of freshly prepared nitroprusside solution and a few drops of sodium hydroxide, when a deep blue colour, readily changing to green, brown and finally to red, is obtained.

ACETALDEHYDE, ETHANAL, CH_3CHO

Laboratory preparation. Acetaldehyde is prepared in the laboratory by the oxidation of ethyl alcohol with sodium dichromate and dilute

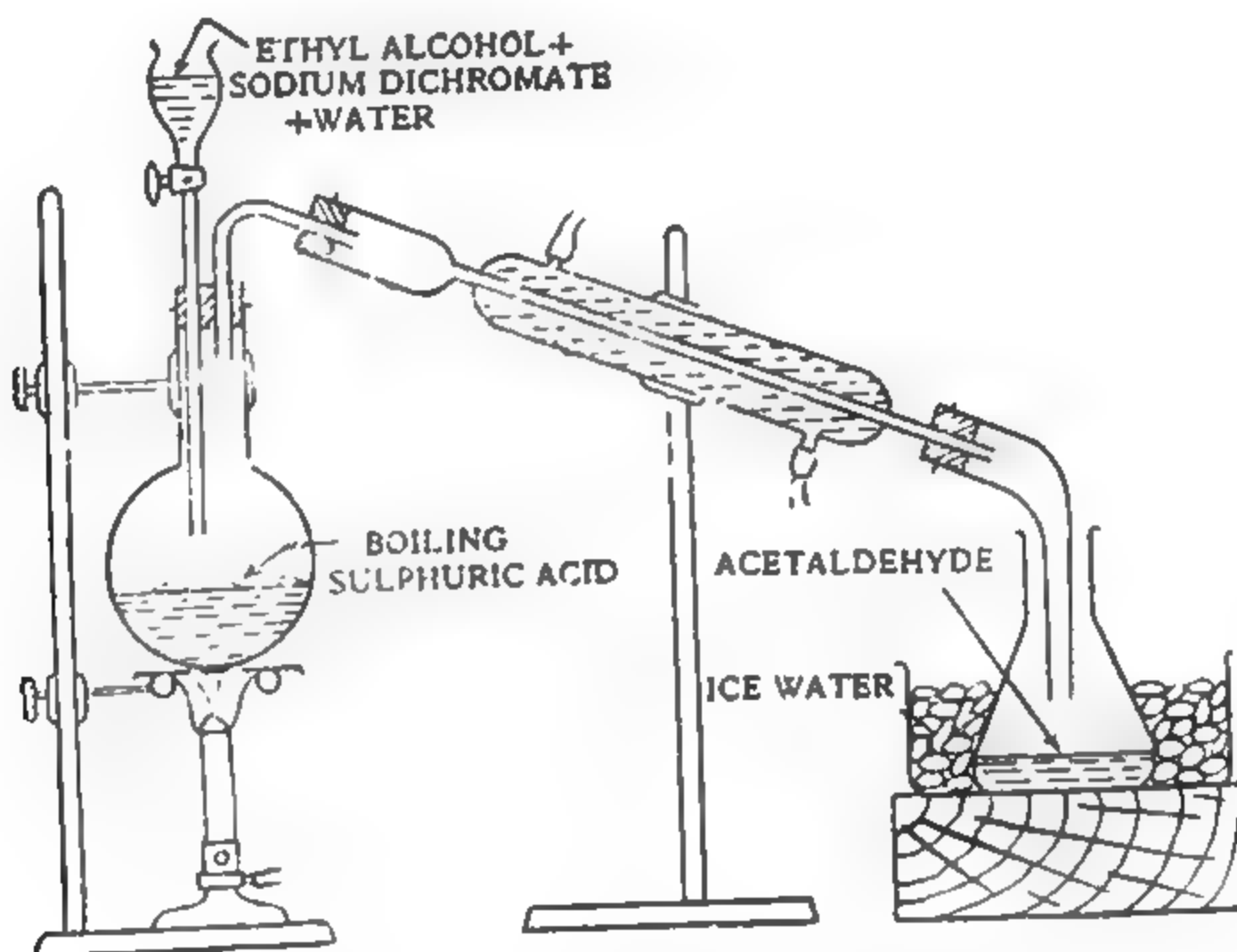


Fig. 2. Laboratory Preparation of Acetaldehyde.

sulphuric acid. An excess of alcohol is used in order to avoid the further oxidation of the aldehyde to acetic acid.

The apparatus used is shown in Fig. 2.

100 ml. of water is mixed with 35 ml. of concentrated sulphuric acid and placed in the round-bottom flask fitted with a dropping funnel and connected to a water condenser. 100 g. of potassium dichromate is dissolved in 100 ml. of water to which 10 ml. of ethyl alcohol is also added. This solution is transferred to the dropping funnel.

The sulphuric acid solution in the flask is heated to boiling and the dichromate solution added gradually from the dropping funnel at such a rate that the reaction mixture in the flask remains boiling. If need be, the burner can be put off.

The distillate consists of a mixture of acetaldehyde, water and some alcohol which is collected in a receiver placed in ice-cold water.

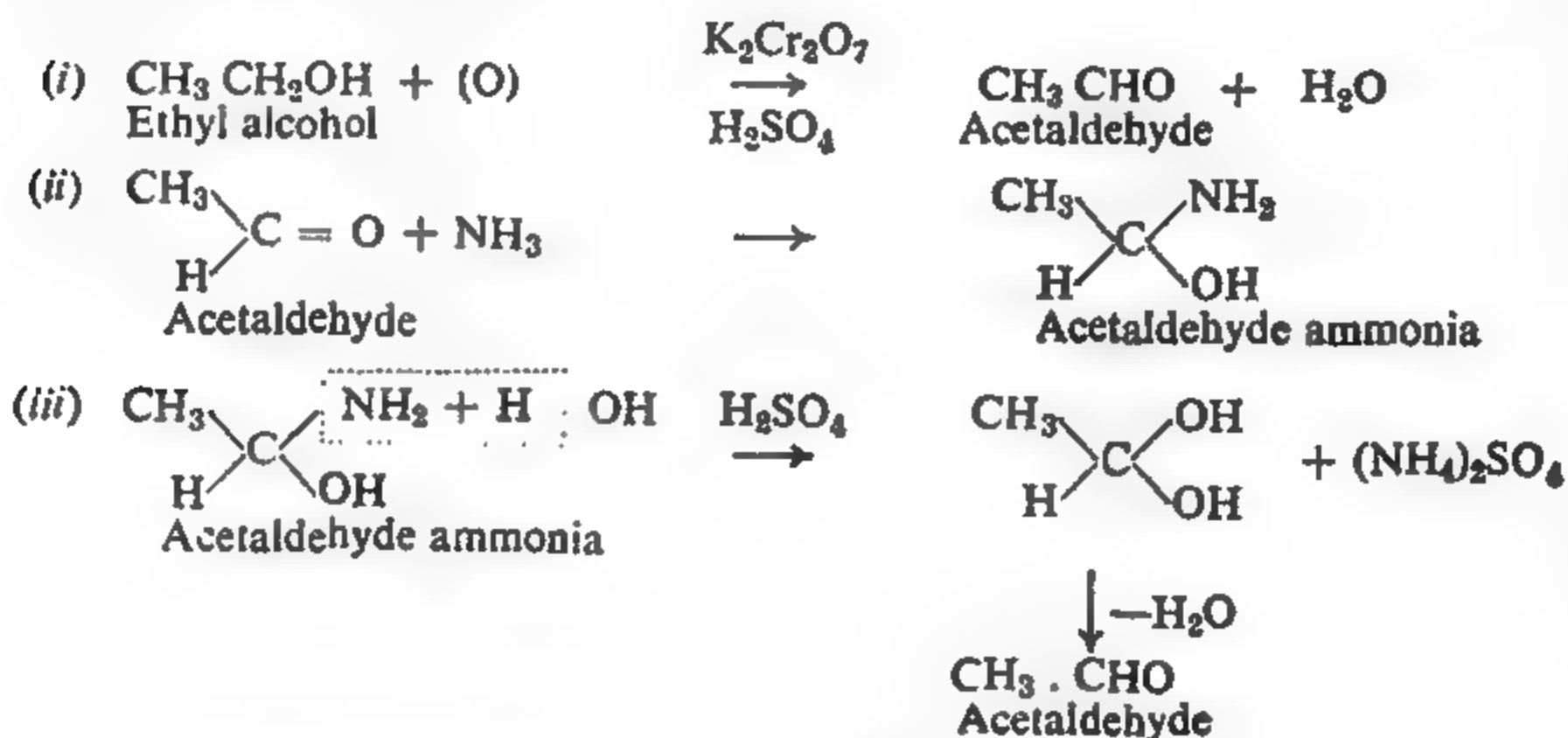
Separation of acetaldehyde. A complete separation of acetaldehyde from the above mixture, by fractional distillation, is not possible. Hence, pure acetaldehyde is obtained by converting it into aldehyde ammonia.

For this purpose, the crude aldehyde obtained above is heated gently on a water bath, in a flask fitted with a water condenser. The upper end of the condenser is connected to a glass tube dipping in ether which is taken in a conical flask placed in a freezing mixture. In 10-15 minutes, most of the aldehyde (b. p. 21°) distils over, leaving behind the water and the alcohol in the flask.

The ether solution of acetaldehyde is then saturated with gaseous ammonia and the solution allowed to stand in a freezing mixture when crystals of acetaldehyde-ammonia separate out.

These crystals are distilled with dilute sulphuric acid on a water bath and the aldehyde evolved is collected in a water cooled receiver. The distillate is dehydrated by adding anhydrous calcium chloride and redistilled.

The various reactions are :

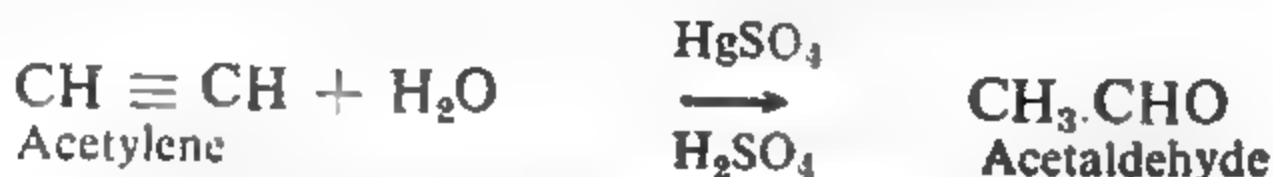


Commercial Preparation Acetaldehyde is prepared on a commercial scale :

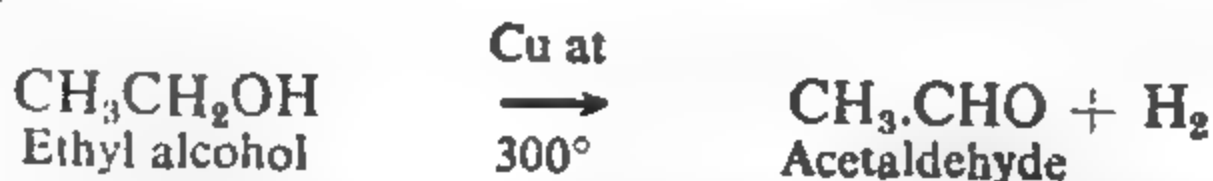
(i) By the catalytic oxidation of ethyl alcohol. A mixture of ethyl alcohol vapour and air is passed over a silver catalyst at 250° .



(ii) By the catalytic hydration of acetylene. Acetylene gas is passed upwards through a hot packed tower, down which flows a solution of 20 per cent sulphuric acid containing a small amount of mercuric sulphate. Acetylene is converted into acetaldehyde.



(iii) By the catalytic dehydrogenation of ethyl alcohol. Alcohol vapours when passed over copper at 300° , lose hydrogen giving acetaldehyde.

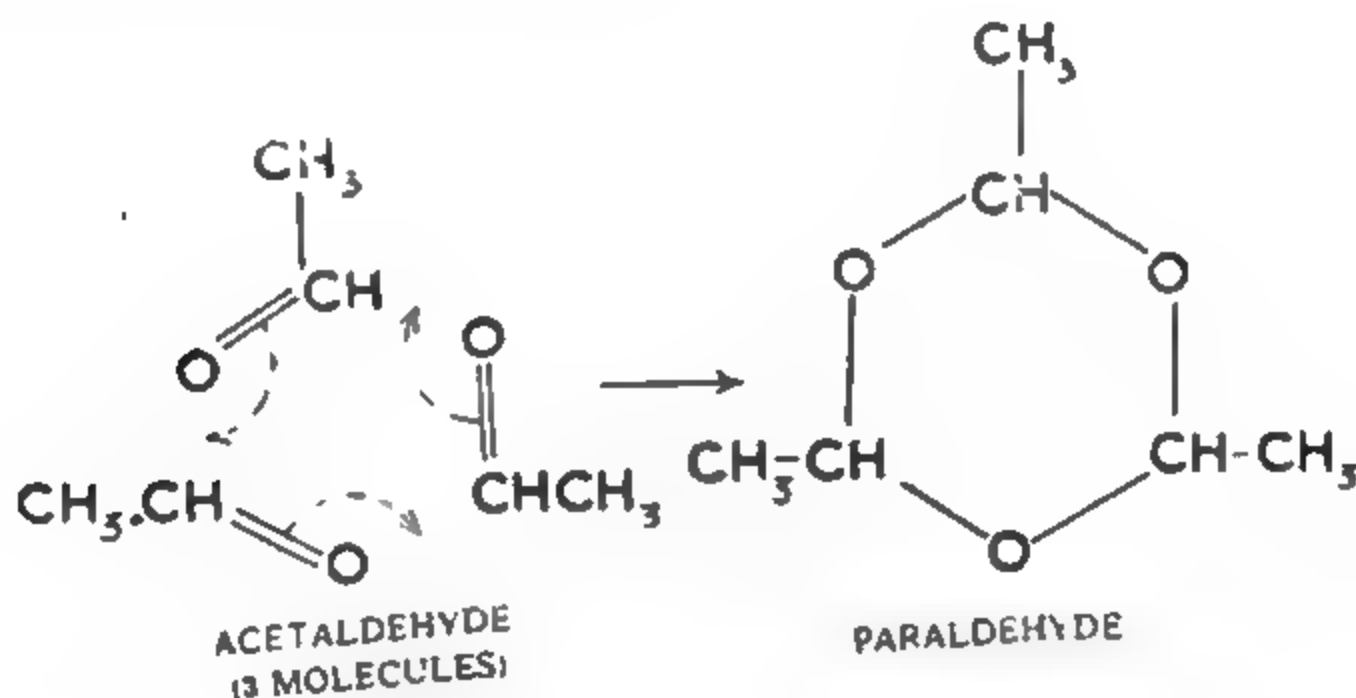


Properties. Acetaldehyde is a colourless, pungent smelling, highly volatile liquid, boiling at 21° . It is miscible with water, ethyl alcohol and ether in all proportions.

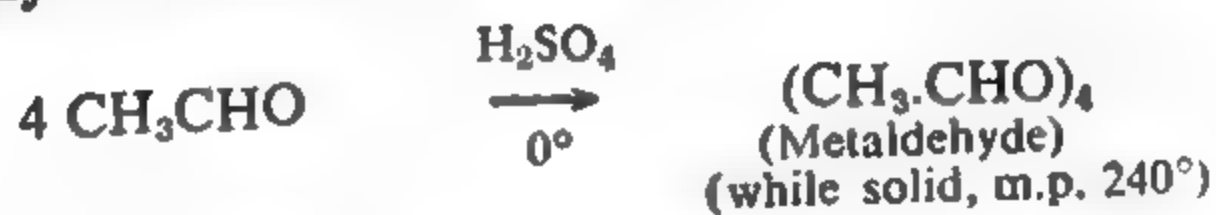
It gives all the reactions characteristic of aldehydes (see general properties).

Polymers of Acetaldehyde. Acetaldehyde readily undergoes polymerisation giving different products under different conditions.

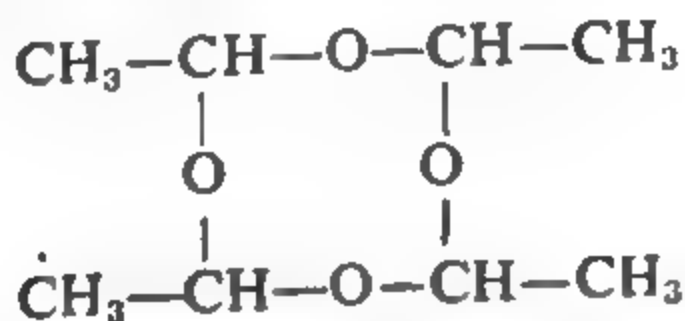
(i) When treated with a few drops of concentrated sulphuric acid, a brisk reaction starts resulting in the formation of paraldehyde $(\text{CH}_3\text{CHO})_3$. It has a cyclic structure.



(ii) When treated with a few drops of concentrated sulphuric acid at 0° , metaldehyde is formed



Metaldehyde is believed to have the following structure.



Uses. (1) The most important use of acetaldehyde is the production of acetic acid and acetic anhydride.

(2) It is also used for the preparation of ethyl alcohol, paraldehyde, *n*-butyl alcohol, etc.

(3) Metaldehyde is used as a portable solid fuel for spirit burners and cookers.

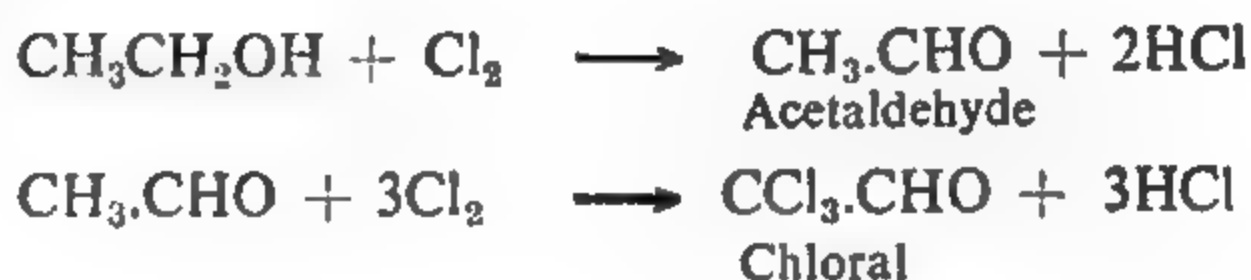
Tests. Acetaldehyde gives the usual tests of aldehyde. Besides, it gives the following specific tests.

(1) It gives a blue colour with sodium nitroprusside and piperidine.

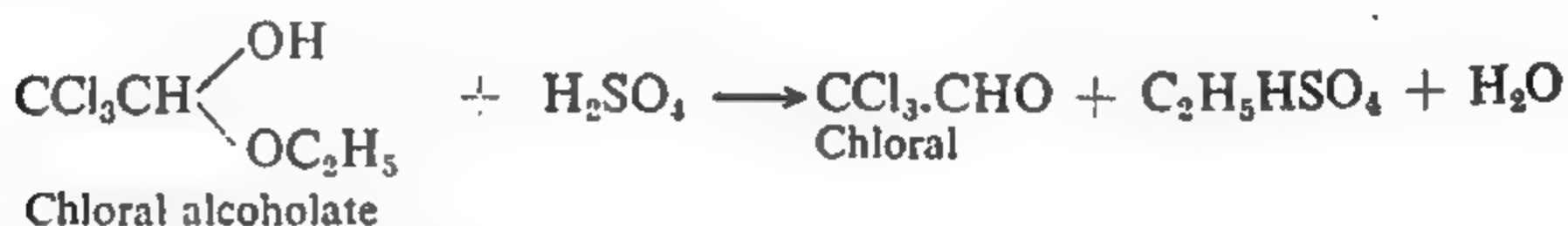
(2) It gives a cherry-red colour with a solution of nitroprusside containing sodium hydroxide.

Chloral, Trichloroacetaldehyde, CCl_3CHO

Chloral is prepared on a commercial scale by the chlorination of ethyl alcohol. Chlorine is passed into ethyl alcohol for many hours, first in the cold and then at 60° . The reactions involved may be represented as below :



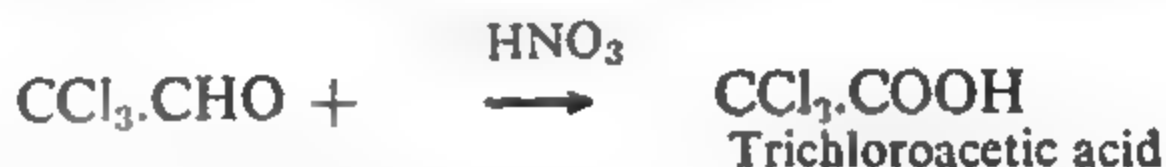
The end product, in fact, is not chloral but chloral alcoholate (a crystalline compound) which is distilled with sulphuric acid to recover alcohol.



Properties. Chloral is a heavy colourless oily liquid having a characteristic pungent odour. It is insoluble in water. It is used as a hypnotic.

Chemically, it gives the usual reactions of aldehydes. It forms addition products with ammonia, hydrogen cyanide, sodium bisulphite and condensation products with hydroxylamine, hydrazine, phenylhydrazine.

It can be easily oxidised with nitric acid to give trichloroacetic acid.



Hence, it acts as a reducing agent as well. Like aldehydes, it reduces Fehling solution and ammoniacal solution of silver nitrate.

When boiled with alkalis, it gives chloroform.



Chloral forms a hydrate with water.



Chloral hydrate is one of the rare organic compounds which are stable, although containing more than one hydroxyl groups attached to the same carbon atom.

ACETONE PROPANONE, CH_3COCH_3

This is the first and the most important member of the series.

Laboratory Preparation. Acetone is prepared in the laboratory by heating calcium acetate.



The apparatus used is shown in Fig. 3.

20 gm. of calcium acetate is placed in a dry hard glass tube connected to a reflux condenser as shown. The other end of the condenser carries an adapter dipping in the receiver.

The tube is carefully heated in the beginning, moving the flame over the tube, in order to avoid its cracking. After some time the tube is heated strongly with full flame. Heating is continued till the reaction is complete and the entire amount of the acetone formed has distilled over.

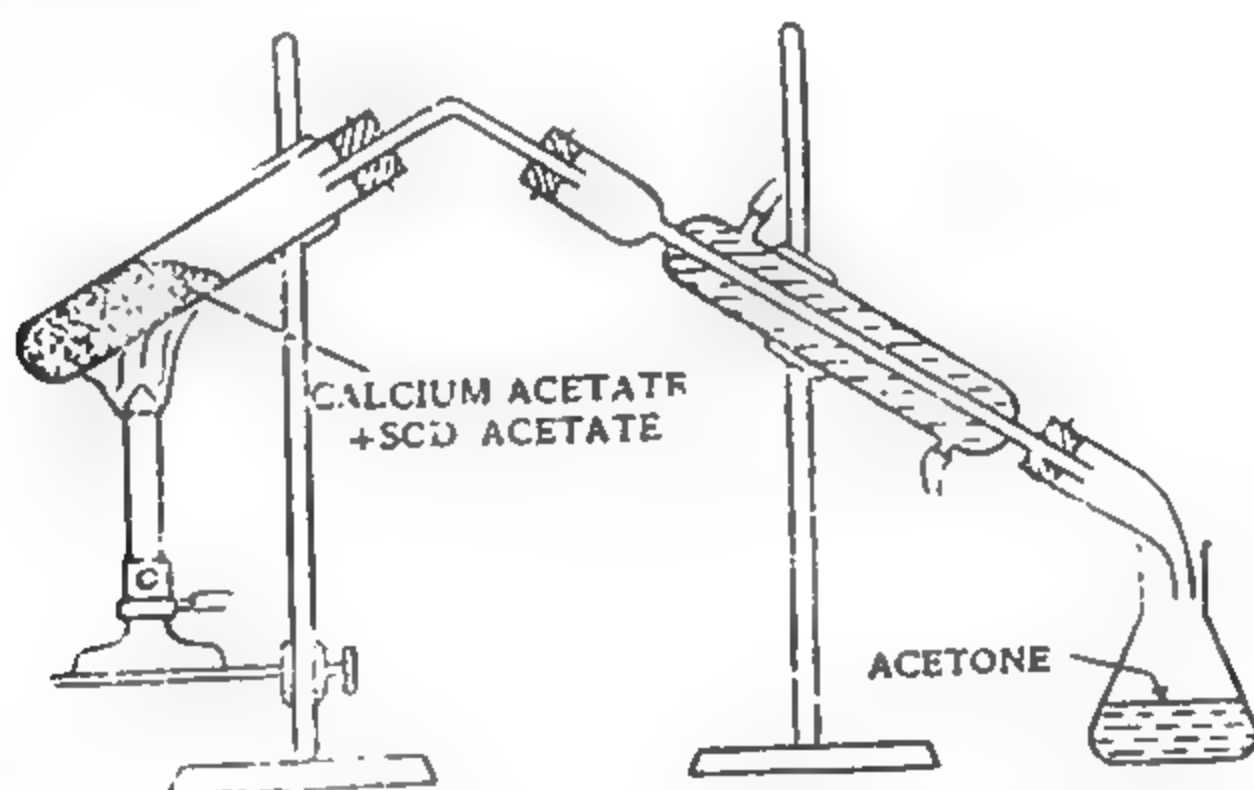
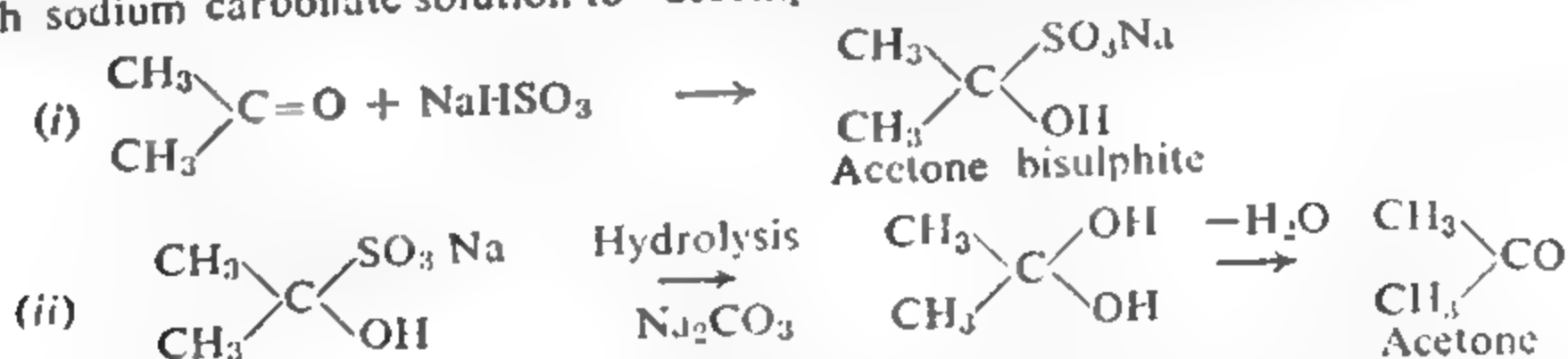


Fig. 3. Laboratory Preparation of Acetone.

The distillate obtained is treated with saturated sodium bisulphite solution when crystals of acetone bisulphite separate out. These crystals are removed and distilled with sodium carbonate solution to decompose the bisulphite to yield acetone.

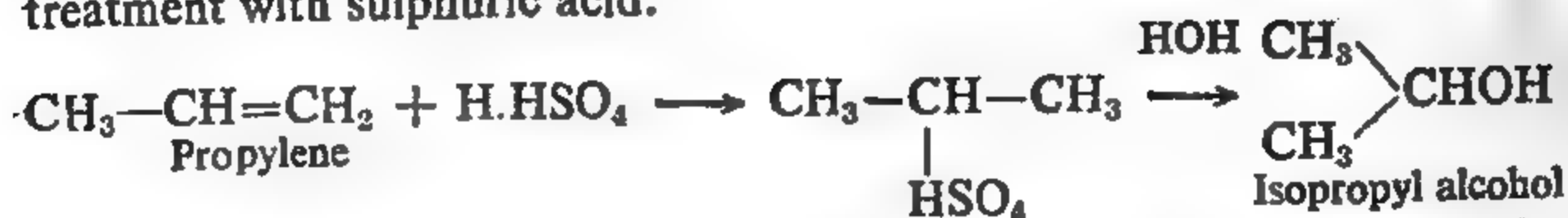


The distillate contains acetone and some water. The latter is removed by adding anhydrous calcium chloride.

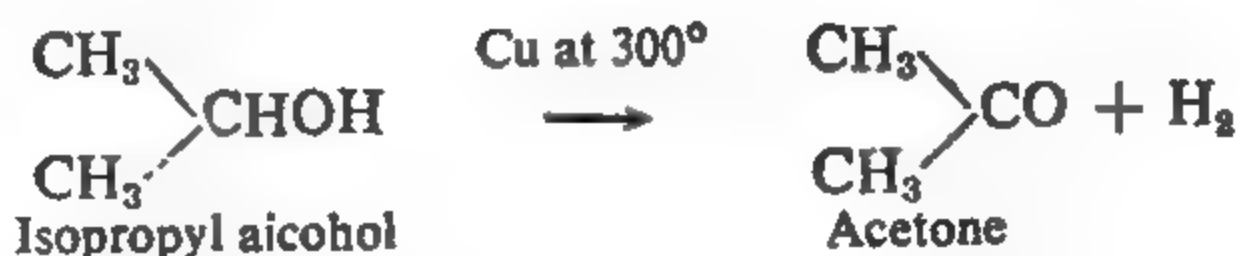
Manufacture. Acetone is prepared on a commercial scale by a number of methods.

(1) **From petroleum products.** Large amounts of propylene obtained from cracking of petroleum, are converted into isopropyl alcohol by

treatment with sulphuric acid.



Isopropyl alcohol is then de-hydrogenated by passing over copper at 300° to give acetone.



(2) **From acetic acid.** Large quantities of acetone are obtained these days from acetic acid. The vapour of acetic acid are passed over calcium oxide or manganous oxide at $300-400^\circ$ to yield acetone.



(3) **From wood distillation.** The crude acetone obtained from wood distillation (*cf.* manufacture of methyl alcohol) is treated with sodium bisulphite, when solid acetone bisulphite is obtained. It is separated and distilled with sodium carbonate solution to recover pure acetone (*cf.* laboratory preparation of acetone).

The calcium acetate obtained from wood distillation can also be converted into acetone.



(4) **Fermentation Process.** Now-a-days, acetone is being prepared by fermentation process. During the fermentation of starch or molasses to *n*-butyl alcohol, which is carried in the presence of *Chlostridium Acetobutylicum*, acetone is obtained as a by-product and is separated by fractionation.

Purification of acetone. The best method of purifying acetone consists in saturating it with sodium iodide at $25-30^\circ$. The solution is cooled to -10° when the compound $\text{NaI} \cdot 3\text{CH}_3\text{COCH}_3$ crystallises out. It is separated and decomposed by warming to 30° when pure dry acetone is obtained.

Properties. Acetone is a colourless liquid with a characteristic pleasant odour. It boils at 56° and is highly inflammable. It is miscible with water, ethyl alcohol and ether in all proportions. Itself it is an excellent solvent.

Chemically, it gives all the reactions of ketones (*cf.* general properties).

Uses. Acetone is extensively used as a solvent for acetylene, cellulose acetate, cellulose nitrate, celluloid, lacquers, etc.

It is used as a starting material for the production of iodoform, chloroform, sulphonal, etc.

Tests. *Legal's test.* About 5 ml. of the aqueous solution of acetone is taken in a test tube and about 1 ml. of sodium hydroxide and a few drops of freshly prepared solution of sodium nitroprusside added to it. A ruby-red colour, fading to yellow on standing, is obtained.

(2) *Iodoform test.* About 2 ml. of the acetone solution is taken in a test-tube and a few drops of ammonium hydroxide added to it. Decinormal solution of iodine is added dropwise when a black precipitate of nitrogen iodide is obtained. On warming, the black precipitate disappears and iodoform is produced which can be detected by its peculiar smell.

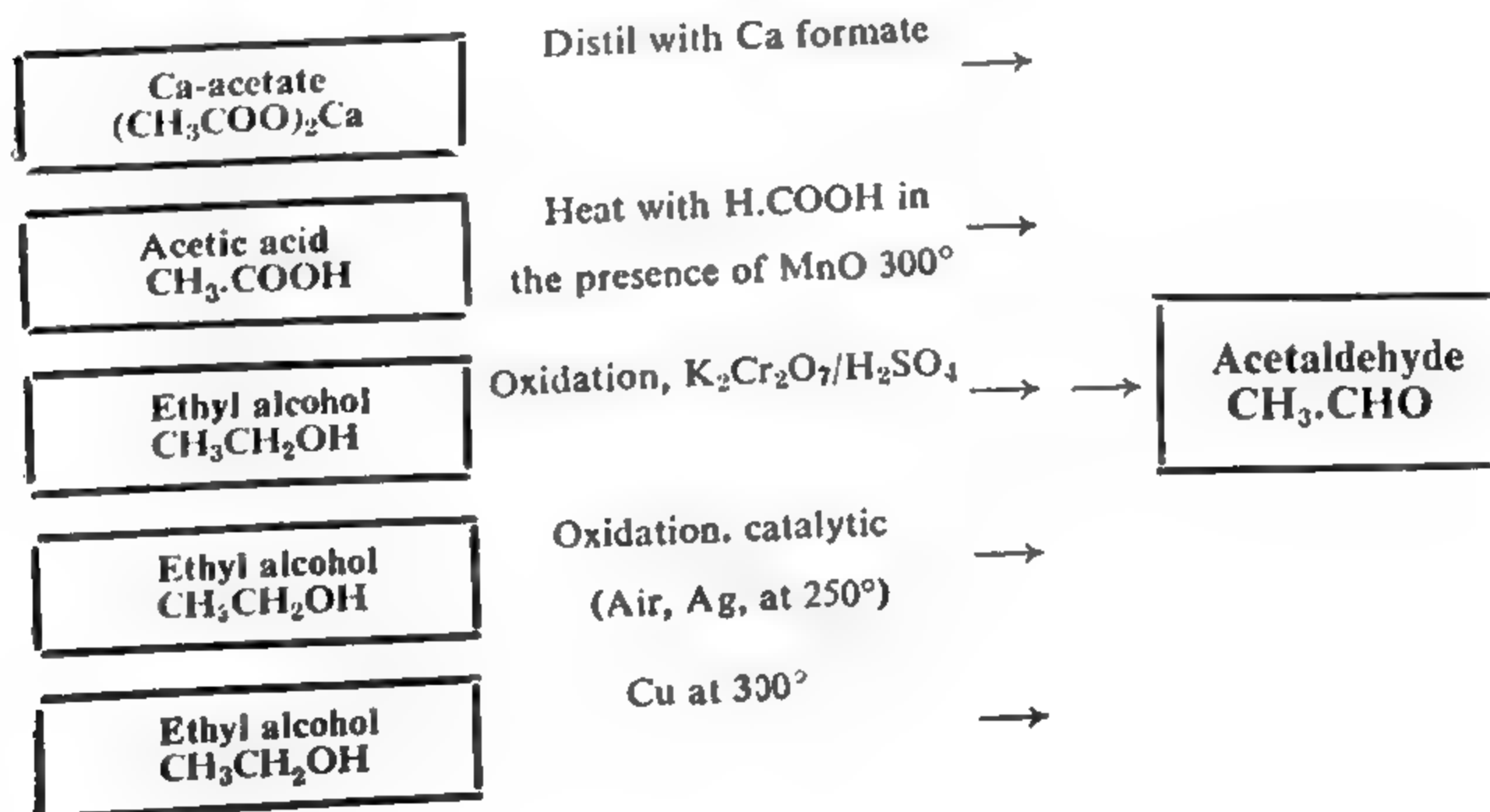
Alcohol does not form iodoform in this manner.

(3) *Indigo test.* A small amount of ortho-nitrobenzaldehyde is dissolved in about 2 ml. of acetone. The solution is transferred to 100 ml. of water containing a little sodium hydroxide and vigorously stirred. A blue colour of indigotin is rapidly produced.

SUMMARIES OF TYPICAL MEMBERS

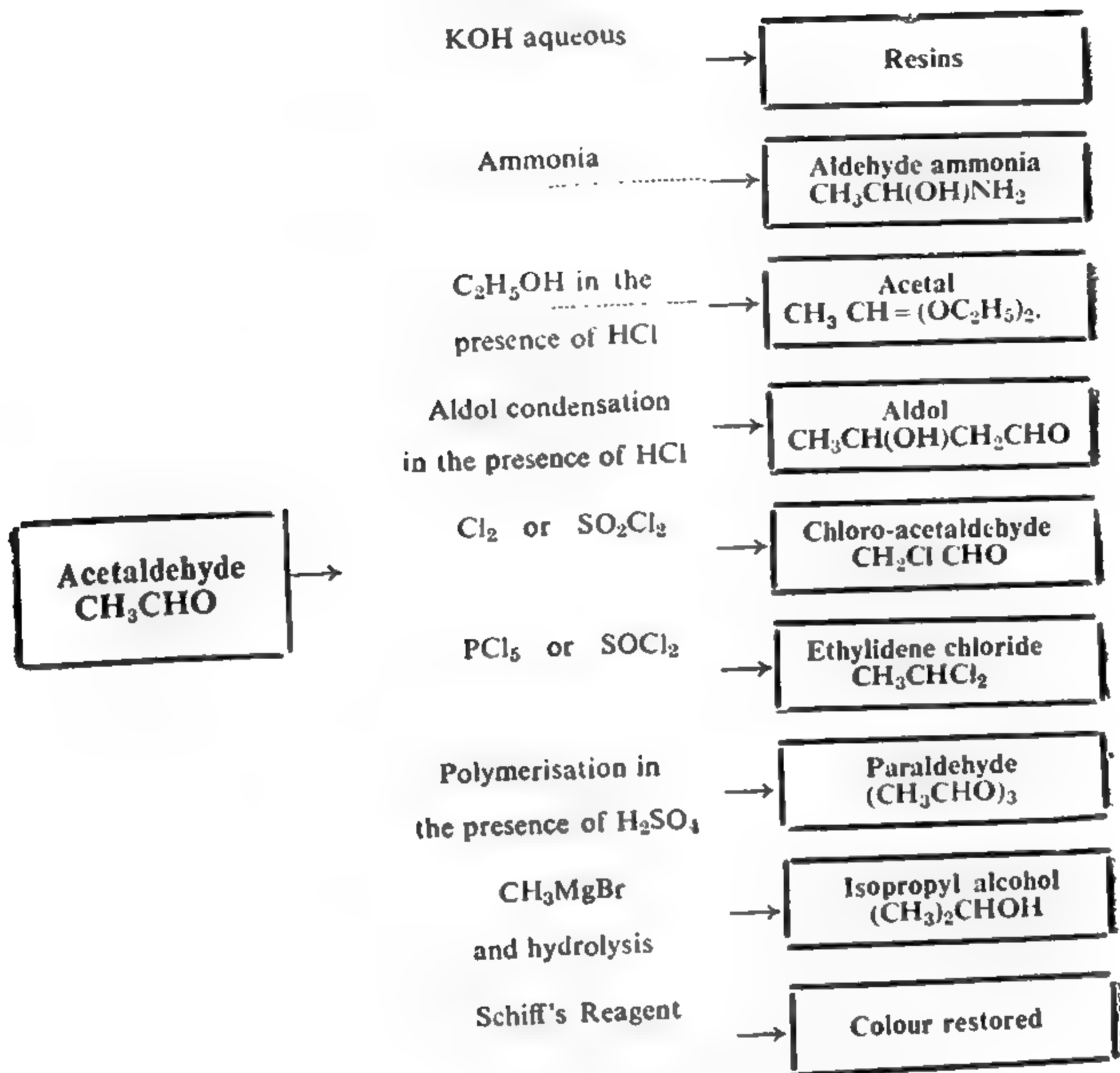
1. PREPARATION AND PROPERTIES OF ACETALDEHYDE

Preparation.



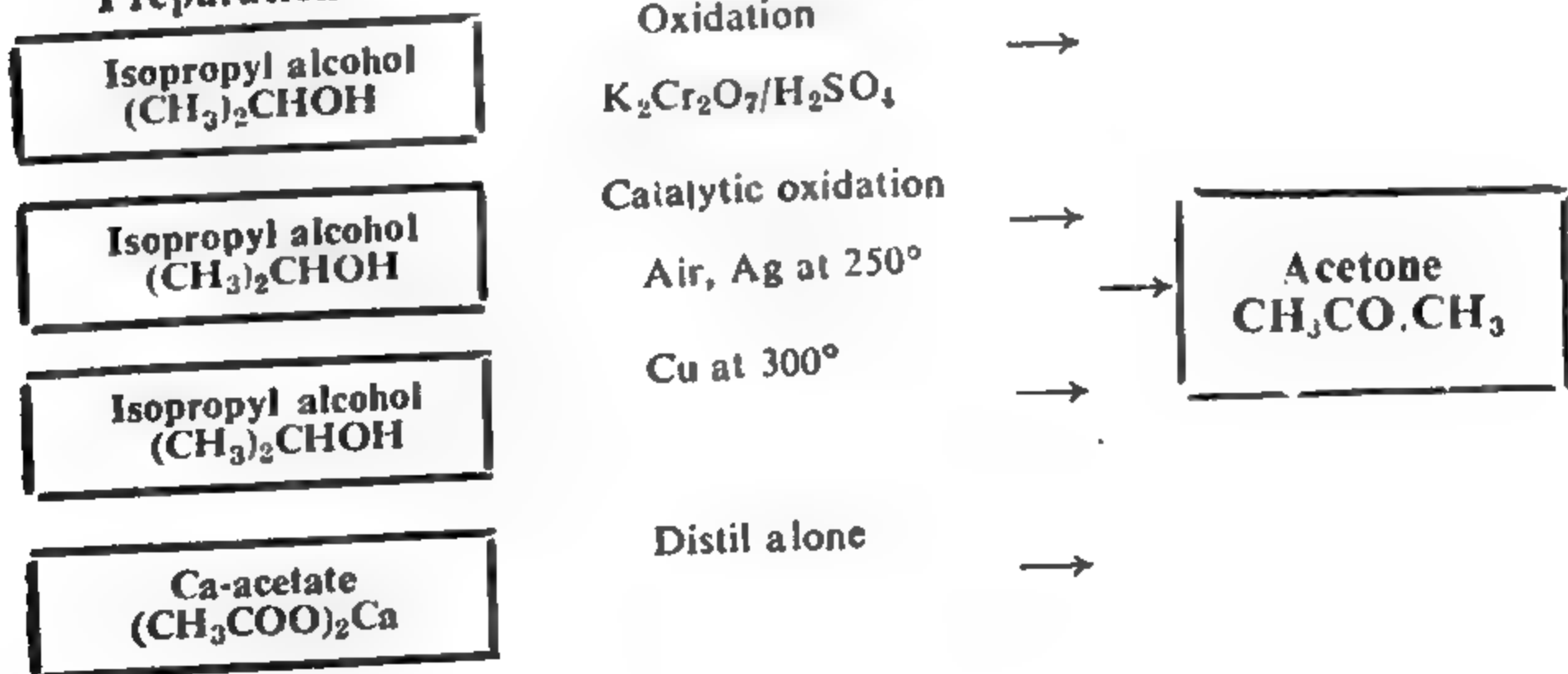
SUMMARIES

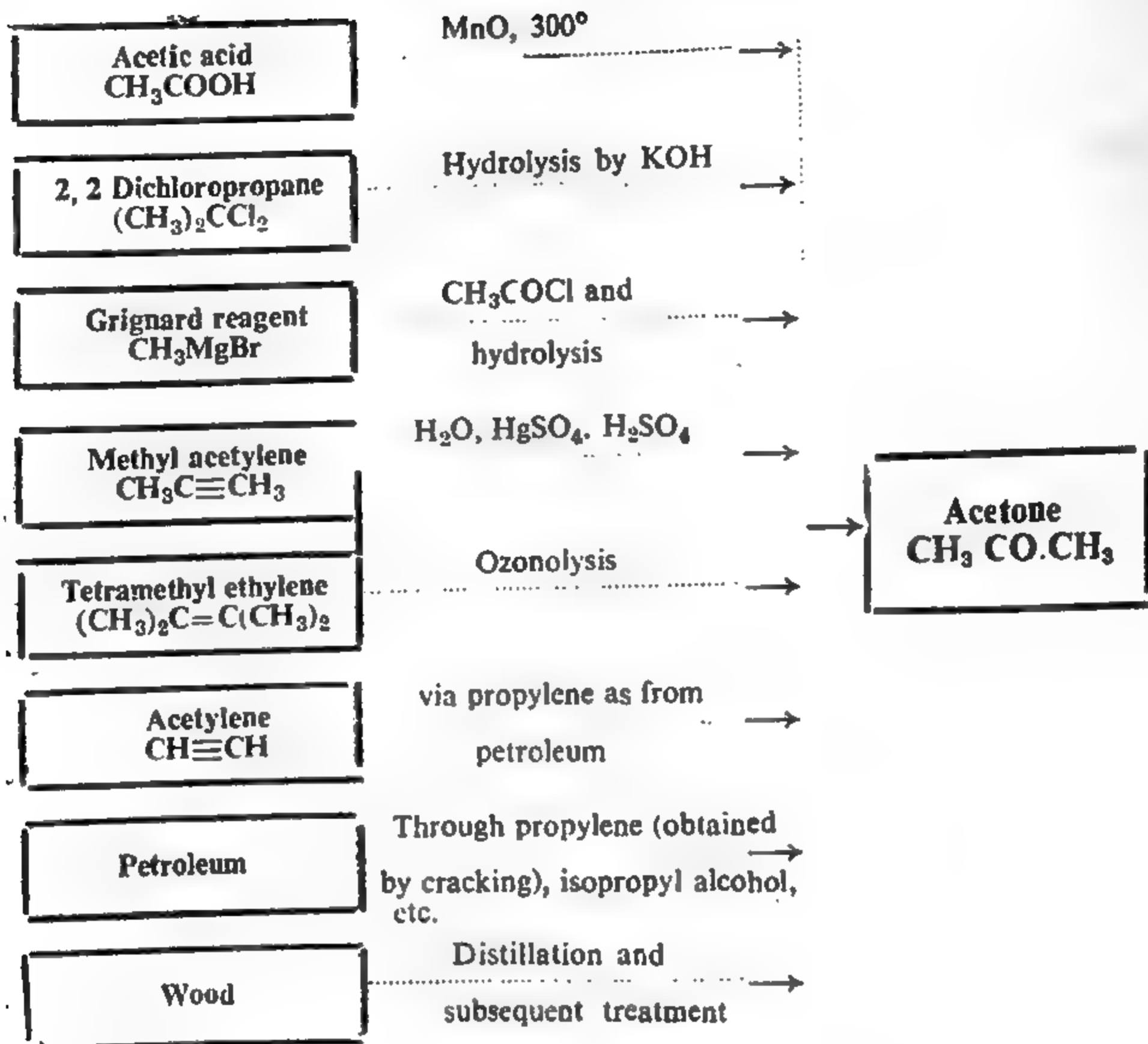
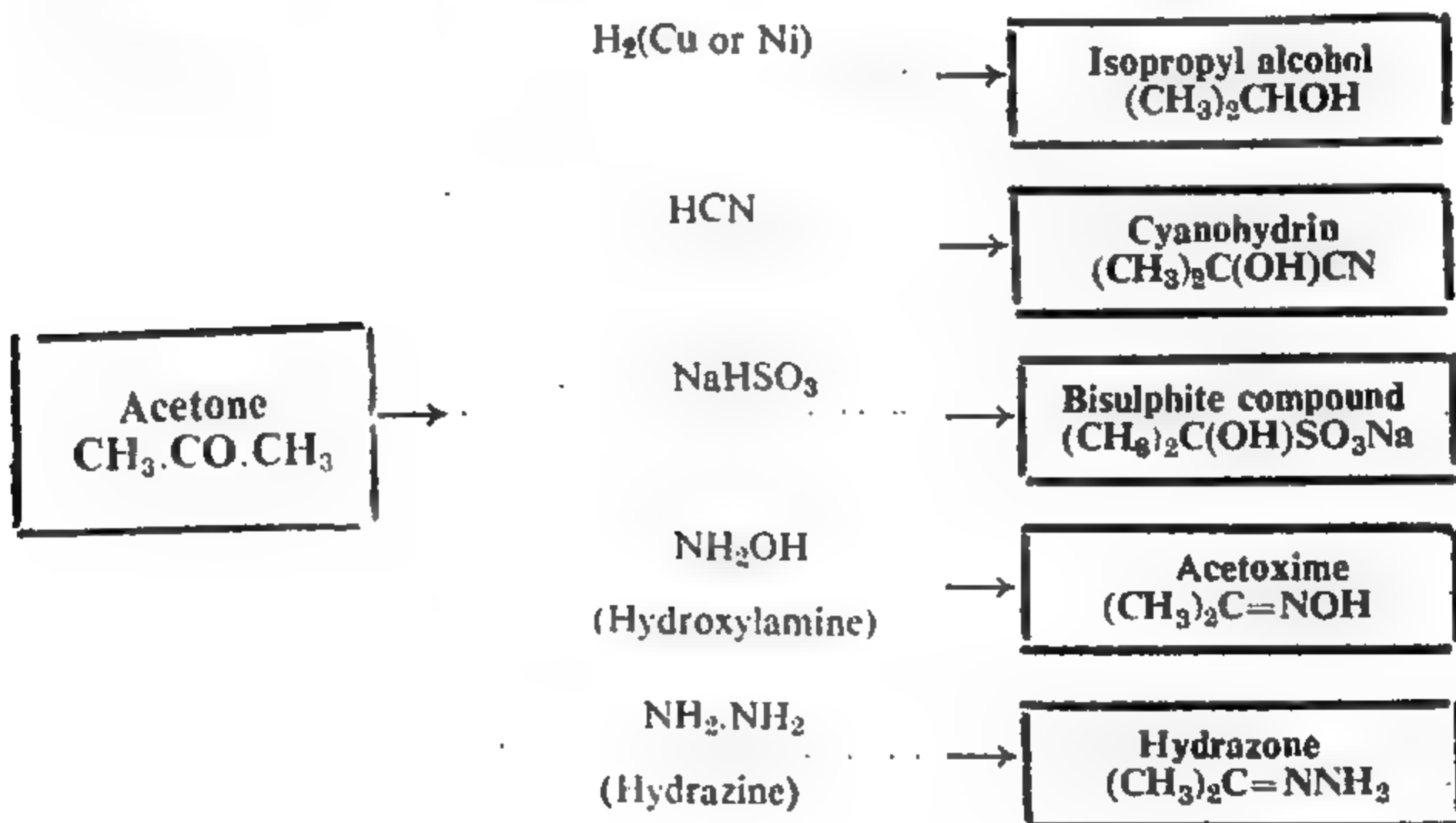
Acetylene $\text{CH}\equiv\text{CH}$	$\text{H}_2\text{O}, \text{HgSO}_4, \text{H}_2\text{SO}_4$	→	
Butylene $\text{CH}_3\text{CH}=\text{CHCH}_3$	Ozonolysis	→	
Acetyl chloride CH_3COCl	Reduction, H_2 , Pd.	→	Acetaldehyde CH_3CHO
Grignard reagent CH_3MgBr	React with HCOOC_2H_5	→	
Ethylidene chloride CH_3CHCl_2	Hydrolysis by CaO suspension	→	
Properties.			
	Addition of H_2 (Ni or Cu)	→	Ethyl alcohol $\text{CH}_3\text{CH}_2\text{OH}$
	Addition of HCN	→	Cyanohydrin $\text{CH}_3\text{CH}(\text{OH})\text{CN}$
	Addition of NaHSO_3	→	Aldehyde bisulphite $\text{CH}_3\text{CH}(\text{OH})\text{SO}_3\text{Na}$
	Condensation with hydroxyl amine (NH_2OH)	→	Acetaldoxime $\text{CH}_3\text{CH}=\text{NOH}$
Acetaldehyde CH_3CHO	Condensation with hydrazine (NH_2NH_2)	→	Hydrazone $\text{CH}_3\text{CH}=\text{N.NH}_2$
	Condensation with $\text{C}_6\text{H}_5\text{NH.NH}_2$	→	Phenyl hydrazone $\text{CH}_3\text{CH}=\text{NHC}_6\text{H}_5$
	Oxidation $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$	→	Acetic acid CH_3COOH
	Fehling solution	→	Red ppt. of Cu_2O
	AgNO_3 ammoniacal	→	Silver mirror

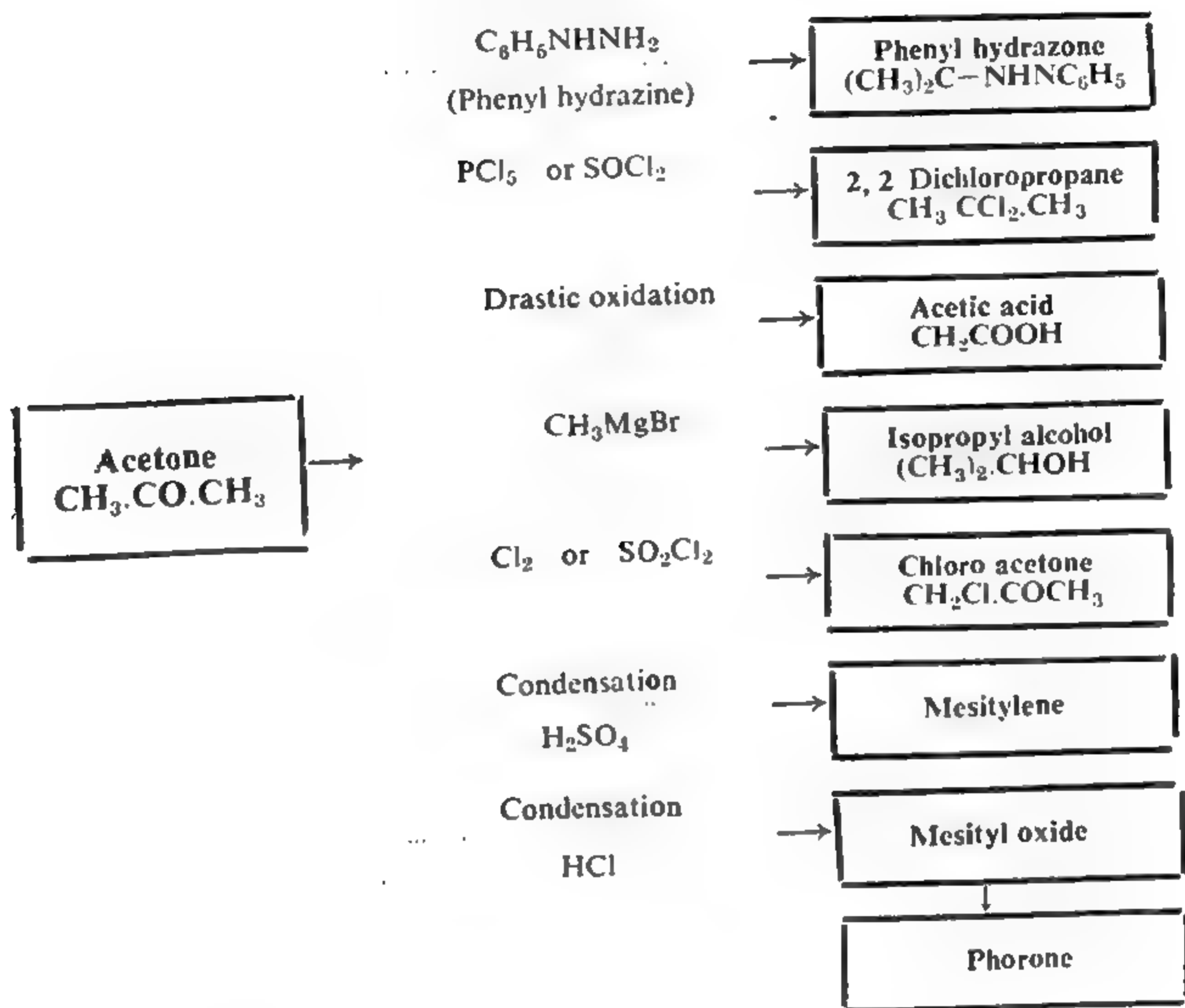


2. PREPARATION AND PROPERTIES OF ACETONE

Preparation.



**Properties.**



QUESTIONS

1. What are aldehydes and ketones? Discuss the structural relationship between the two types of compounds.
2. Describe the general methods of preparation of aldehydes and ketones. Which of these methods can be used for the industrial preparation of acetaldehyde and acetone?
3. Compare and contrast the properties of aldehydes and ketones. To what do they owe their characteristic behaviour? (Panjab Inter 1952)
4. What are aldehydes and ketones? How can they be distinguished from each other?
5. What is a carbonyl group? Describe the characteristic reactions associated with this group.
6. 'Because of the presence of the common carbonyl group, in their structure, aldehydes and ketones exhibit a number of common properties.' Justify the above statement.
7. Describe in detail : (i) the addition reactions (ii) the replacement reactions.
8. Explain the term 'condensation'. Describe the various condensation reactions of aldehydes and ketones.

9. How is formaldehyde prepared (i) in the laboratory, (ii) on an industrial scale? How would you differentiate formaldehyde from other aldehydes? Write a brief note on the polymers of formaldehyde.
10. How is formalin obtained? To what uses is it put? What specific tests would you apply for its identification?
11. Describe in detail the laboratory preparation of acetaldehyde. How would you distinguish it from formaldehyde?
12. Describe the various methods for the commercial preparation of acetaldehyde. Compare and contrast the properties of acetaldehyde with those of acetone.
13. Describe the important methods used for the production of acetone on an industrial scale. Mention its important uses.
14. How is chloral prepared? Describe its properties and uses. How does chloral react with water and ethyl alcohol?
15. Give five general methods of preparing aldehydes and two chemical properties and two uses of formaldehyde.
16. Enumerate various tests by which aldehydes can be differentiated from ketones. (Panjab Inter 1957)
17. Give general methods of preparing aldehydes and their important reactions. (Panjab Inter 1955)
18. Give the formula, physical state and some outstanding properties of the following : (a) Formaldehyde. (b) Acetone. (Panjab Inter 1954)
19. To what class of organic compounds does a substance with a molecular formula C_3H_6O belong? How can such compounds be obtained and what are their usual reactions. (Panjab Inter 1950, 1946)
20. Starting from acetaldehyde how would you obtain the following :
(a) Ethyl alcohol (b) Chloroform (c) Acetic acid (d) Acetone (e) Methane
(f) Formaldehyde (g) Acetylene (h) Ethylidene chloride (i) Aldehyde-oxime and
(j) Aldehyde phenylhydrazone. (Panjab Inter 1948)
21. Give the preparation and important properties of acetaldehyde. How can it be distinguished from formaldehyde and acetone? (Panjab Inter 1948)
22. Explain what is meant by Addition, Polymerisation and Condensation. Illustrate your answer from aldehydes and ketones. (Panjab Inter 1964)

CHAPTER XXXV

CARBOXYLIC ACIDS

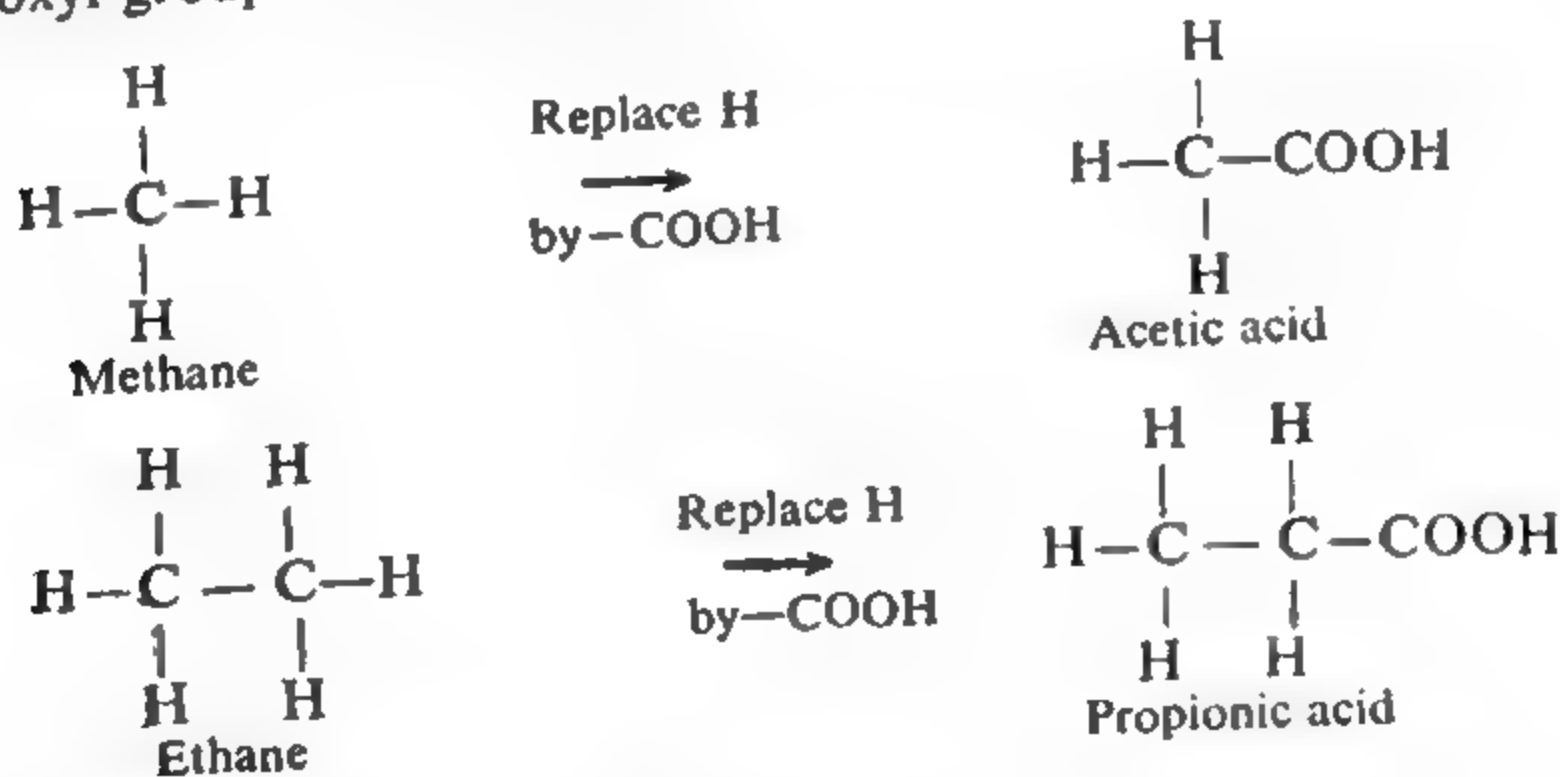
Carboxylic acids are compounds having the carboxyl group, —COOH .

A little consideration shows that the group —COOH ($\text{—}\overset{\text{O}}{\parallel}\text{C—OH}$) is made up of a carbonyl group and a hydroxyl group. The compounds containing the carboxyl groups are, therefore, called **carboxylic acids**. They are further designated as mono, di or tricarboxylic acids depending upon whether one, two or three carboxylic groups are contained in a molecule of the carboxylic acid.

MONOCARBOXYLIC ACIDS

The saturated monocarboxylic acids are commonly known as **fatty acids**. The name has been derived from 'fat' as many of these acids, particularly the higher members, are obtained from fats.

The monocarboxylic acids may also be regarded as derived from the corresponding alkanes by the replacement of one hydrogen atom by the carboxyl group. For instance,



The general formula of the series is $\text{C}_n\text{H}_{2n+1}\cdot\text{COOH}$ or $\text{R}\cdot\text{COOH}$ where R may be H or any alkyl radical.

The names of a few members of the series are given below :

Formula	Common name	I. U. C. name
H.COOH	Formic acid	Methanoic acid
CH ₃ .COOH	Acetic acid	Ethanoic acid
C ₂ H ₅ .COOH	Propionic acid	Propanoic acid
C ₃ H ₇ .COOH	Butyric acid	Butanoic acid
C ₄ H ₉ .COOH	Valeric acid	Pentanoic acid

Sometimes, these acids are also named as *alkyl derivatives of acetic acid*.

For example,

CH ₃ CH ₂ .COOH	Methyl acetic acid
CH ₃ .CH ₂ .CH ₂ .COOH	Ethyl acetic acid
$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH} - \text{COOH} \end{array} $	Dimethyl acetic acid
(CH ₃) ₃ C.COOH	Trimethyl acetic acid and so on,

General Methods of preparation. The following methods are available for the preparation of fatty acids :

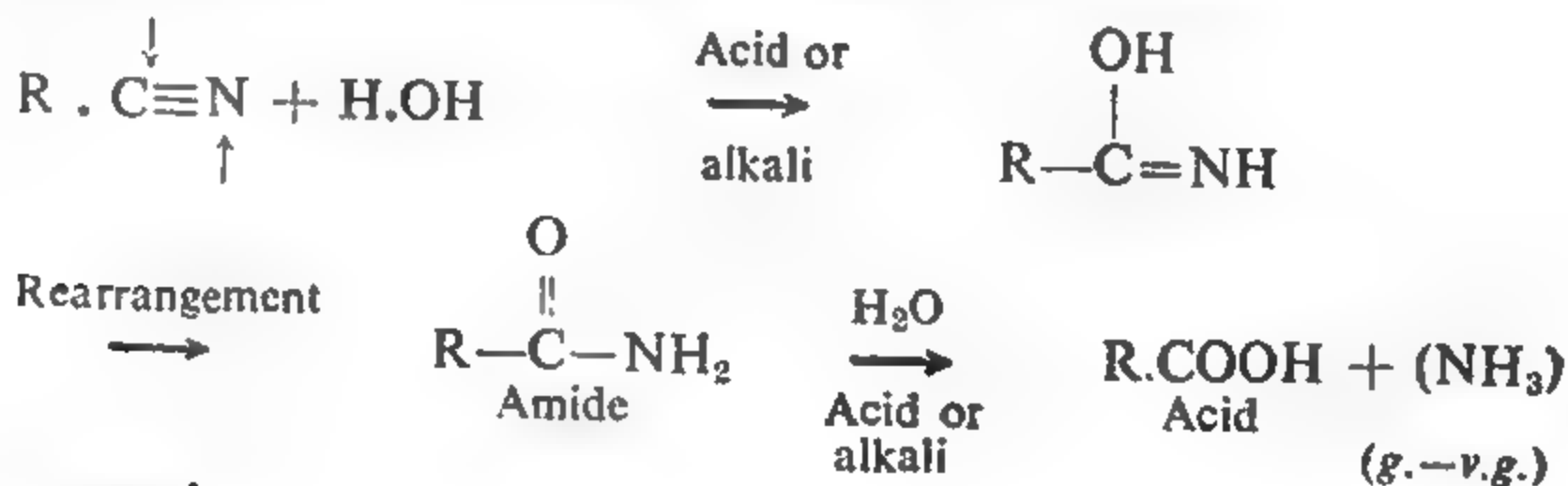
(1) By the oxidation of alcohols and aldehydes. Primary alcohols and aldehydes on *oxidation with acid dichromate* yield fatty acids.



For example,



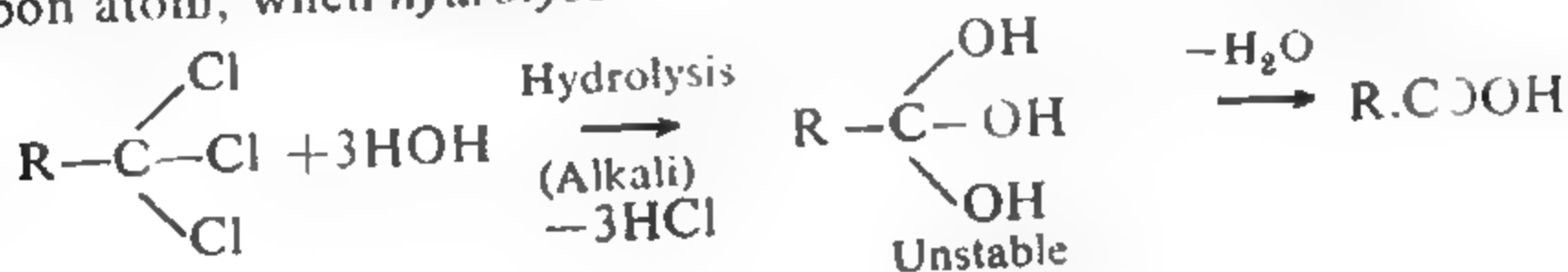
(2) By the hydrolysis of alkyl cyanides. Alkyl cyanides, when *hydrolysed with mineral acids or alkalies*, produce acids.



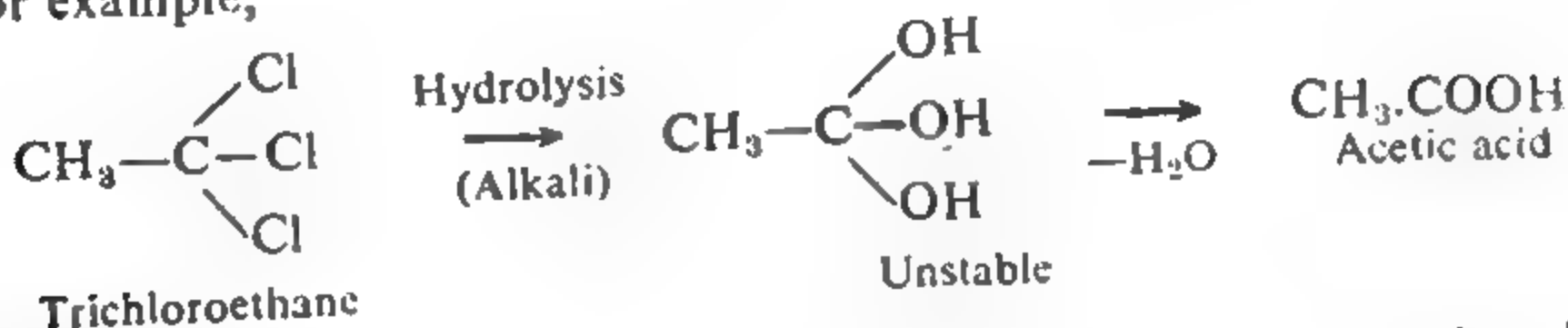
For example,



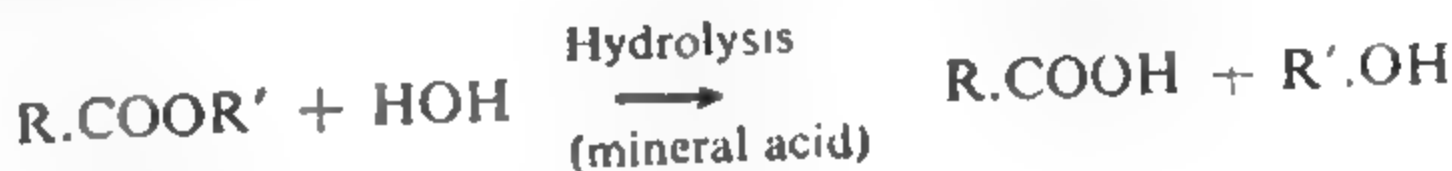
(3) **By the hydrolysis of trihalogen derivatives of alkanes.** Trihalogen derivatives in which all the three halogen atoms are linked to the same carbon atom, when *hydrolysed with an alkali*, yield fatty acids.



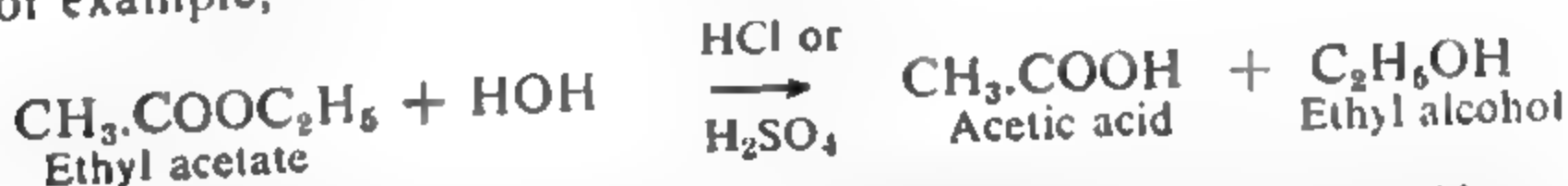
For example,



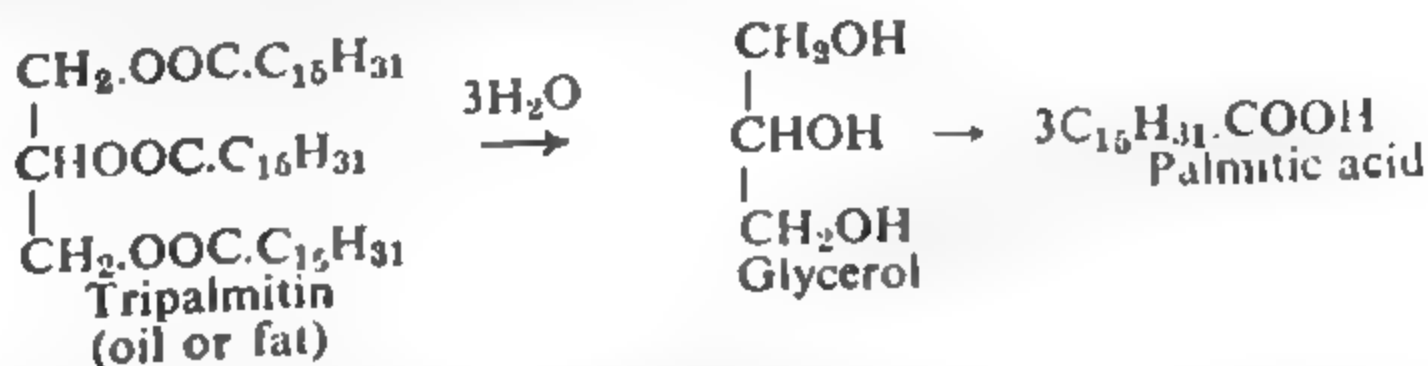
(4) **By the hydrolysis of esters.** Esters when *hydrolysed by mineral acids* yield fatty acids.



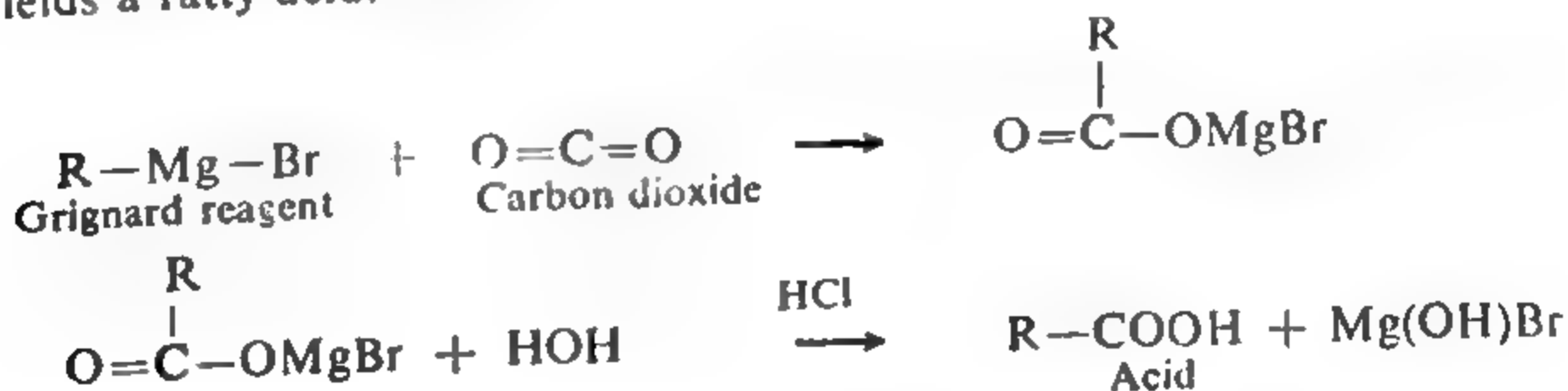
For example,



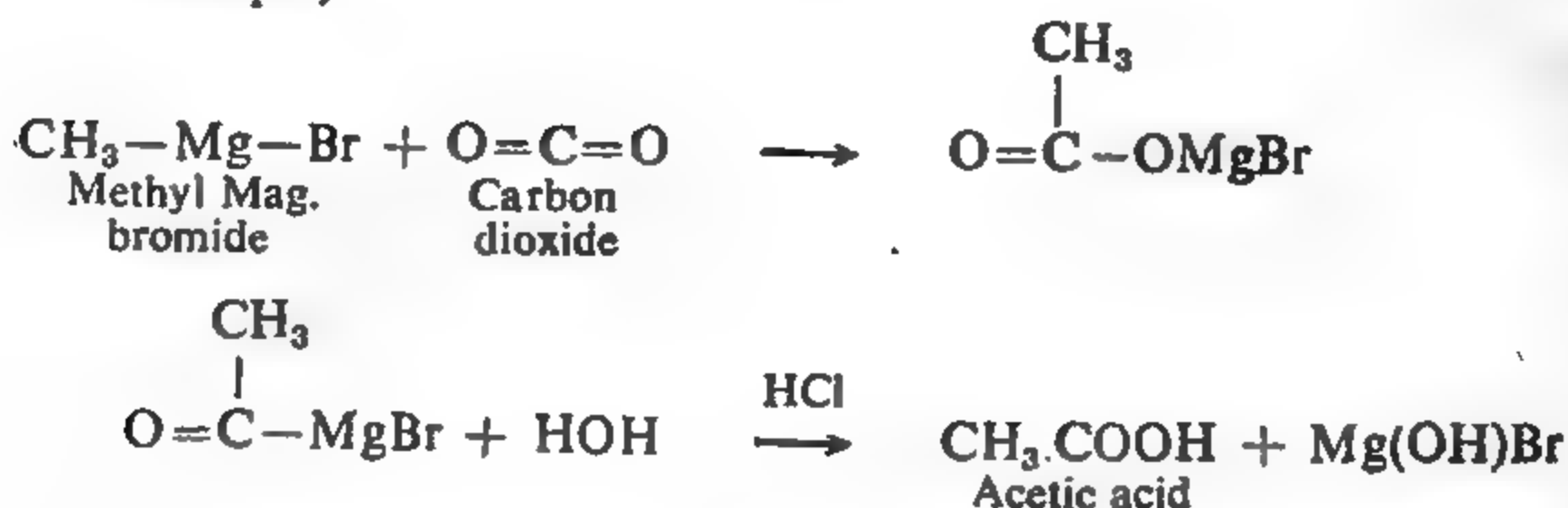
This method is particularly useful for the preparation of higher fatty acids, such as palmitic acid ($\text{C}_{16}\text{H}_{31}\text{.COOH}$), stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$), from oils and fats which are triesters of glycerol. For instance.



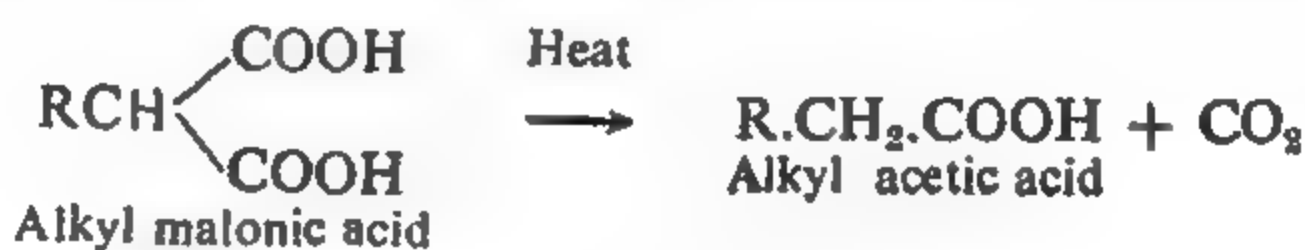
(5) **By the action of carbon dioxide on Grignard reagents.** An ethereal solution of a Grignard reagent easily absorbs carbon dioxide forming an addition product which on subsequent hydrolysis with a mineral acid yields a fatty acid.



For example,



(6) **By heating dicarboxylic acids.** The dicarboxylic acids of the malonic acid series on *heating* lose a molecule of carbon dioxide giving fatty acids.



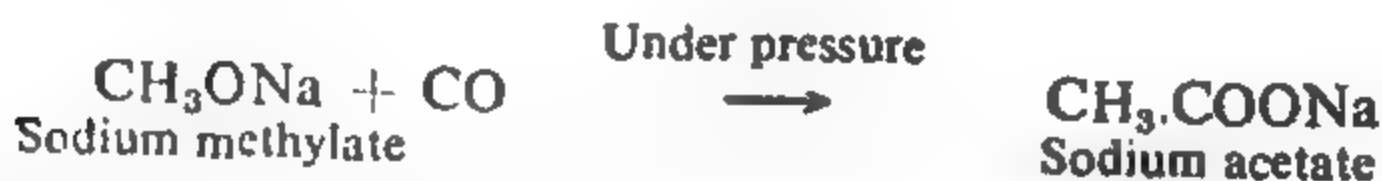
For example,



(7) **By the action of carbon monoxide on sodium alcoholate.** (i) The sodium salt of a fatty acid can be obtained by *heating* sodium alcoholate with carbon monoxide *under pressure*.



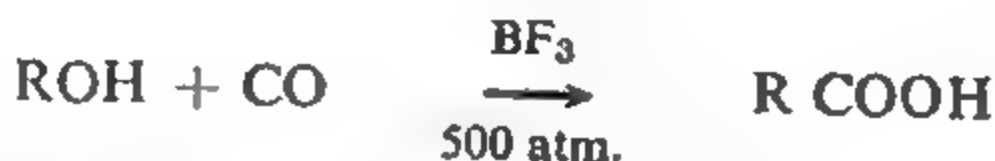
For example,



The sodium salt is then hydrolysed with a mineral acid to yield the acid.

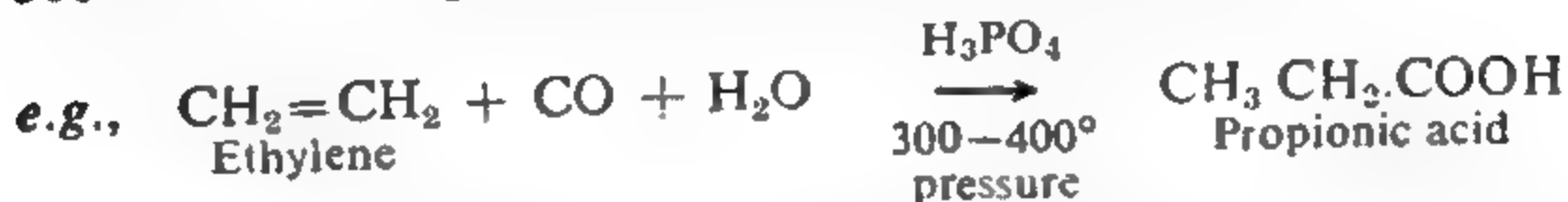


(ii) Instead of sodium salt, the fatty acids as such can also be obtained by *heating* the alcohol with carbon monoxide *at 125–180° under a pressure of 500 atmospheres*, in the presence of *boron trifluoride* as a catalyst.



(8) Recently, monocarboxylic acids have been prepared from olefins by *heating* the latter with carbon monoxide and steam *under pressure at*

300–400° in the presence of *phosphoric acid as catalyst*.



Physical Properties. The first three members of the series are colourless liquids with a pungent smell, readily soluble in water. The acids from C_4 to C_6 are oily liquids with an odour of rancid butter, sparingly soluble in water while the higher members are colourless, odourless waxy solids insoluble in water. All the fatty acids are readily soluble in alcohol and ether.

Chemical Properties. The chemical reactions of acids are due to :

(a) *The carboxyl group*, and (b) *the alkyl radical*.

(a) **Reactions of the Carboxyl Group.**

(1) **Formation of salts.** The fatty acids are easily attacked by strongly electropositive metals when the H-atom is replaced by the metal, resulting in the formation of salts.



For example,



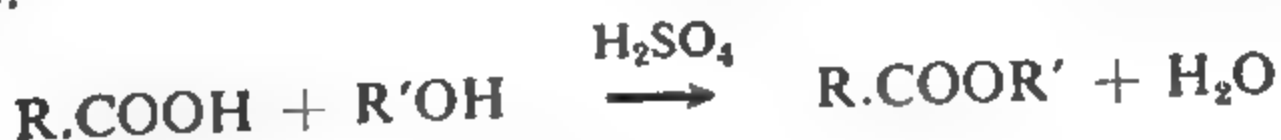
Salts are also formed on interaction with alkalies, when the H-atom of the carboxyl group is replaced by the corresponding metal atom.



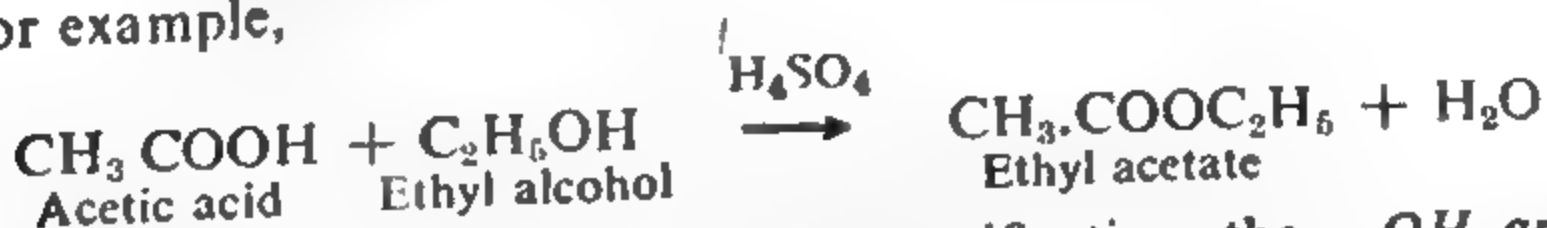
For instance,



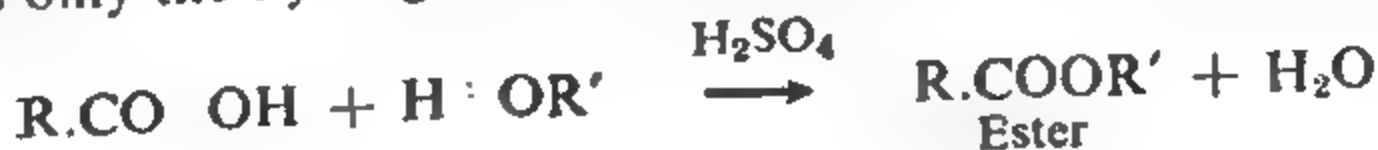
(2) **Formation of esters.** On heating with alcohol in the presence of a dehydrating agent (for instance, sulphuric acid), the fatty acids form esters.



For example,



It is important to note that during esterification, the $-\text{OH}$ group is supplied by the acid and not by the alcohol (see page 348). The latter supplies only the hydrogen so that the mechanism of esterification is



(3) **Formation of acid chlorides.** When treated with phosphorus pentachloride or thionyl chloride, the fatty acids yield acid chlorides by the replacement of the —OH group by chlorine atom.



For example,



(4) **Formation of amides.** When treated with ammonia, the fatty acids give the ammonium salts which on heating lose a molecule of water giving amides.



For instance,



The amides can also be obtained by treating the acid first with phosphorus pentachloride (or thionyl chloride) and then reacting the acid chloride with ammonia.



(5) **Formation of anhydrides.** When heated with acid chlorides, the sodium salt of the fatty acids readily yield the anhydrides.



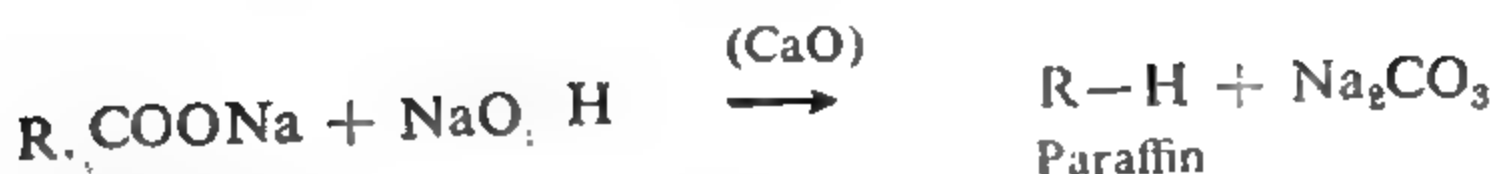
For example,



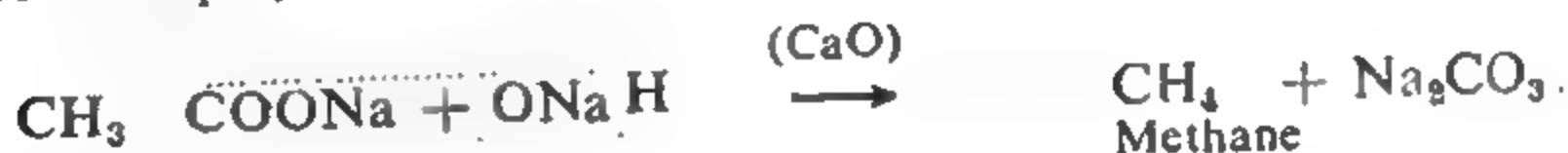
The anhydrides can also be obtained by heating the fatty acid alone in the presence of a strong dehydrating agent such as phosphorus pentoxide.



(6) **Formation of paraffins.** (i) The sodium salts of fatty acids when heated with soda lime, yield paraffins.



For example,



Sodium acetate

(ii) The solutions of sodium or potassium salts of a fatty acids, on electrolysis, give paraffins.



For example,



(7) Formation of aldehydes and ketones. (i) If the calcium salt of a fatty acid (except formic acid) is heated alone it gives a ketone.



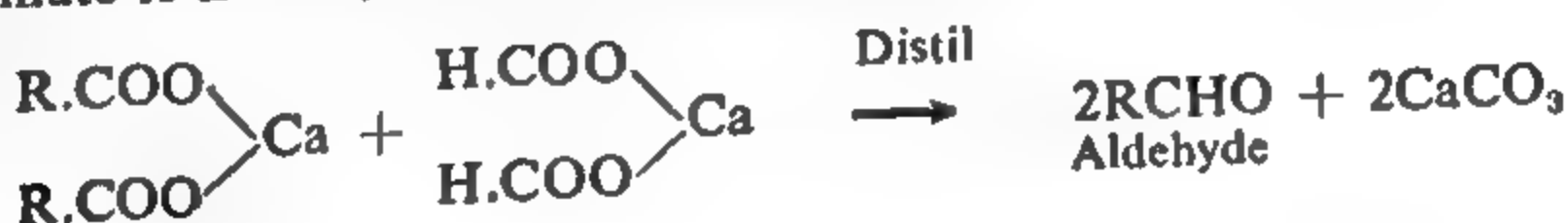
For example,



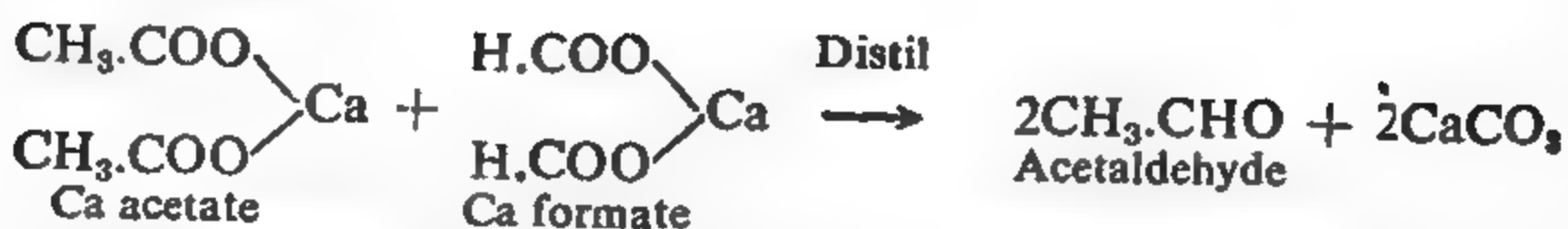
(ii) If the calcium salt of formic acid alone is heated, formaldehyde is obtained.



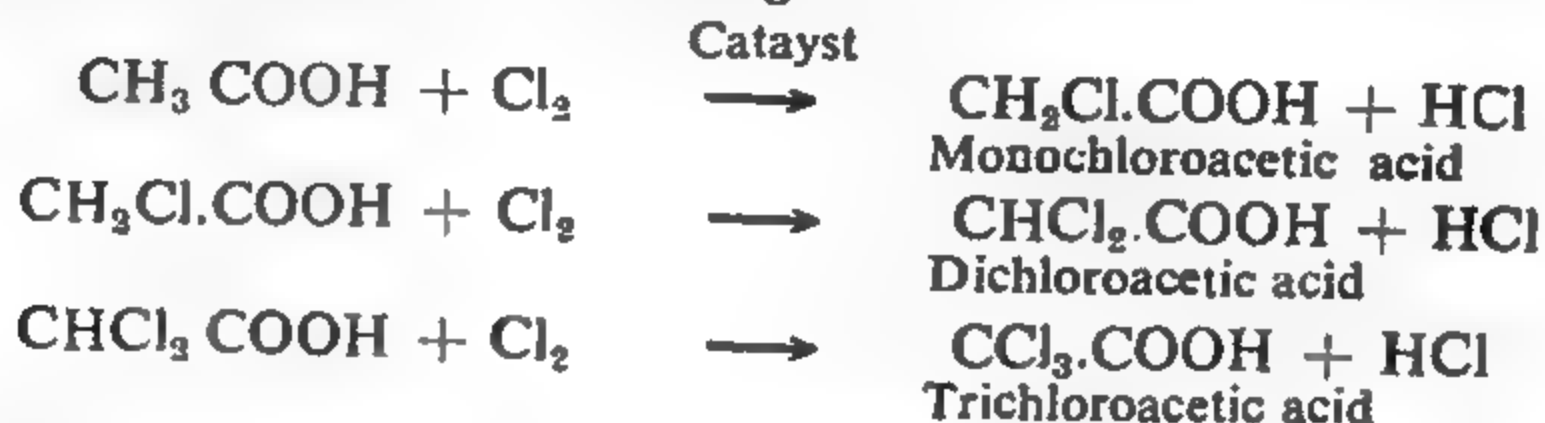
(iii) If a mixture of the calcium salt of the fatty acid and calcium formate is heated, aldehydes are obtained.



For example,



(b) **Halogenation.** With chlorine or bromine in the presence of phosphorus or iodine (catalyst) all the three hydrogens of acetic acid are successively replaced by the halogens.



Tests for carboxyl group. A carboxyl group in a substance may be detected by following tests :

1. The aqueous solution of the acid turns blue litmus red.
2. With sodium bicarbonate, effervescence is produced with the evolution of carbon dioxide.
3. On warming with alcohol and concentrated sulphuric acid, a fruity smell of an ester is obtained.
4. On distilling with soda lime, inflammable vapour of a hydrocarbon are obtained. The residue in the test-tube will give effervescence with dilute mineral acids.

INDIVIDUAL MEMBERS

FORMIC ACID, METHANOIC ACID, HCOOH

Formic acid was prepared for the first time in 1670 by the distillation of red ants and hence the name formic acid (Latin, *Formicus*—ant).

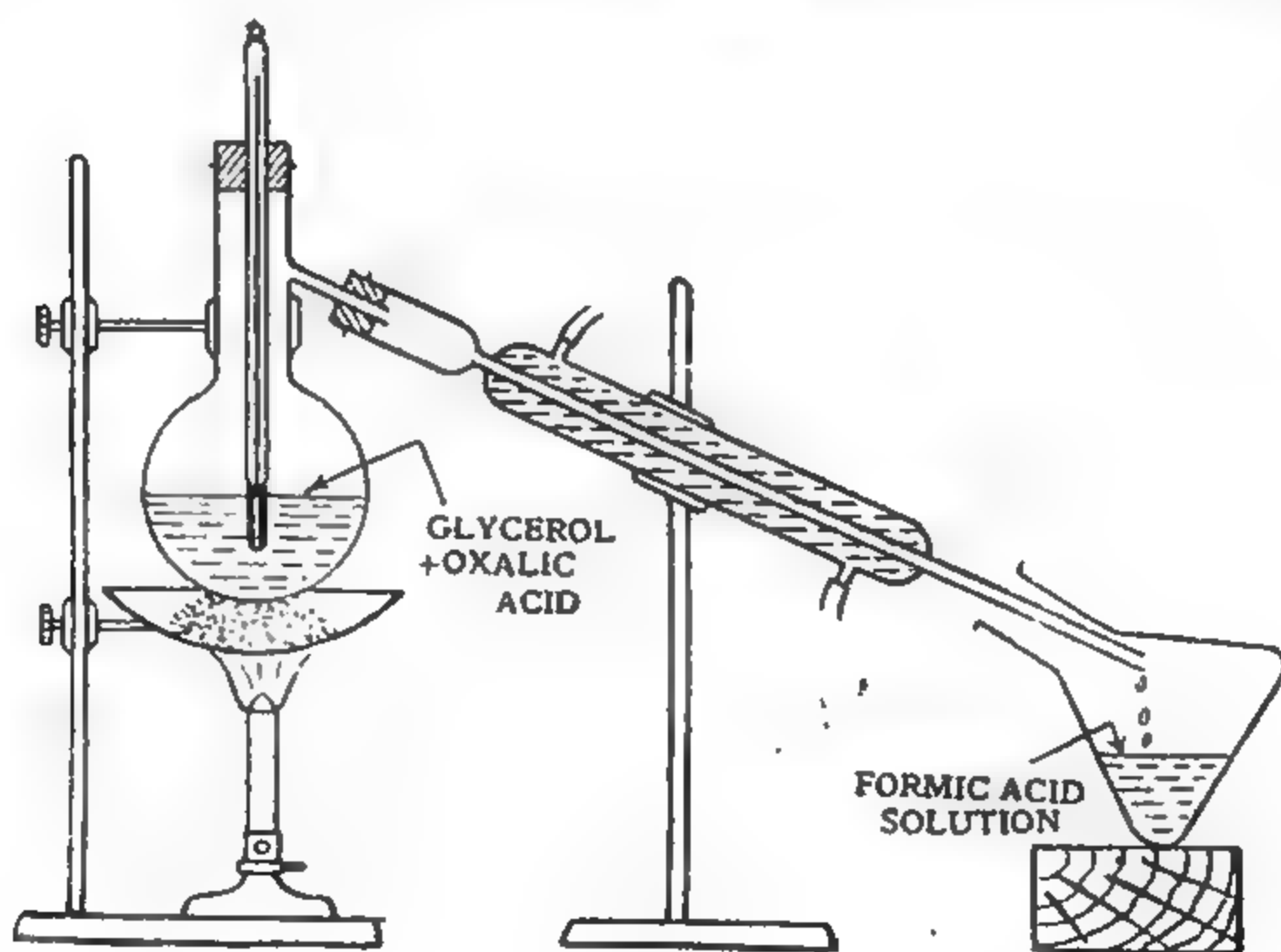


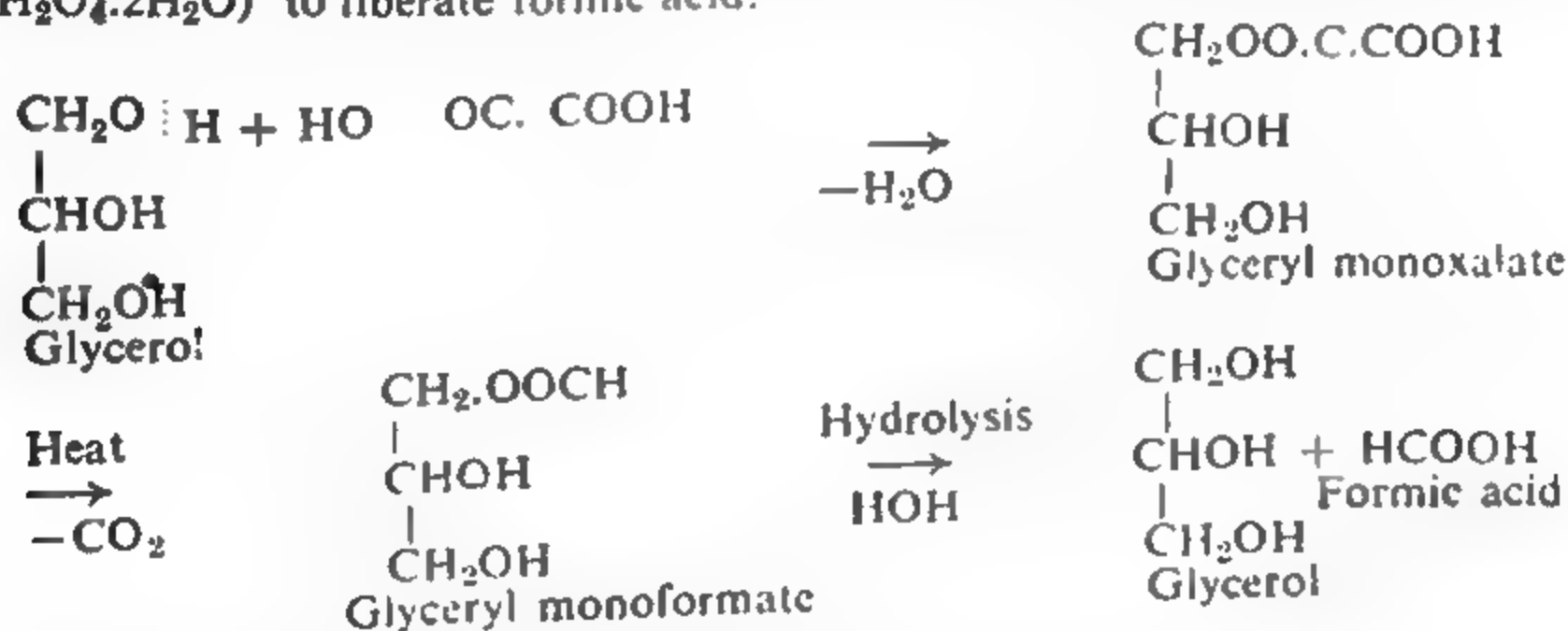
Fig. 1. Laboratory preparation of formic acid.

It also occurs in stinging nettles, bees and wasps and in traces in urine and perspiration.

Laboratory Preparation. Formic acid is best prepared by heating oxalic acid with glycerol at 120° .

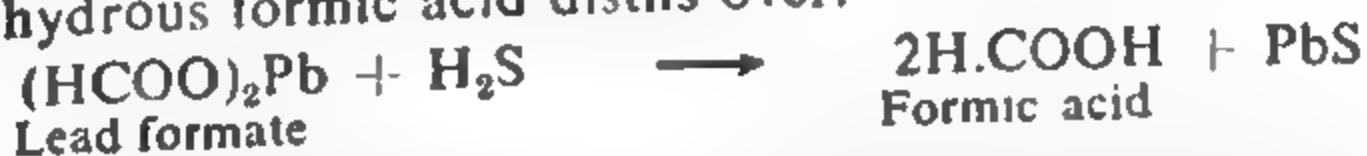
30 ml. of anhydrous glycerol is taken in a distillation flask and about 30 gm. of oxalic acid added to it. The flask is fitted with a thermometer and a water condenser (Fig. 1.) The bulb of the thermometer should dip in the reaction mixture. The flask is heated on a sand bath till the temperature reaches 120° . A vigorous effervescence takes place with the evolution of carbon dioxide. When the reaction slackens, the flask is cooled and another 30 gm. of oxalic acid added to it. The temperature is again raised to 120° when aqueous formic acid begins to distil over.

Reactions. During the first stage of the reaction glycerol forms the monoxalate which on heating, loses a molecule of carbon dioxide giving glyceryl monoformate. In the second stage, with the addition of more of oxalic acid and reheating, the glyceryl monoformate is hydrolysed by the water of crystallisation of oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) to liberate formic acid.



The glycerol set free is used over and over again.

Anhydrous Formic Acid. The aqueous solution of formic acid cannot be fractionated to get anhydrous formic acid because its boiling point (100.5°) is so close to that of water. Hence in order to get anhydrous formic acid the aqueous solution of formic acid obtained is neutralised with lead carbonate and the solution so obtained is filtered and evaporated to get crystals of lead formate. These crystals are dried and heated at 100° in a current of hydrogen sulphide, when anhydrous formic acid distils over.



The formic acid so obtained may contain a small amount of hydrogen sulphide which is eliminated by redistilling the acid over lead formate.

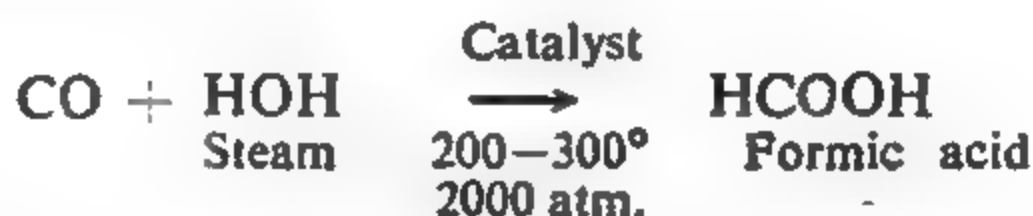
Industrial Preparation. Formic acid is prepared industrially by heating sodium hydroxide and carbon monoxide in an autoclave at 210° under a pressure of 6–10 atmospheres. A quantitative yield of sodium formate is obtained.



The sodium formate obtained above is distilled with sodium hydrogen sulphate when anhydrous formic acid is obtained as the distillate.

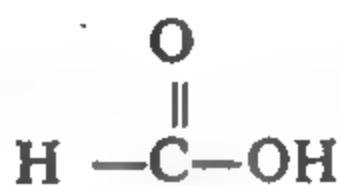


Recent method Now-a-days, formic acid is prepared on a large scale by using steam instead of sodium hydroxide. A mixture of carbon monoxide and water is passed over a *catalyst (ammonium iodide adsorbed on charcoal)* at $200-300^\circ$ under a very heavy pressure of about 2000 atmospheres.



Physical Properties. Formic acid is a colourless liquid boiling at 100.5° . It has a pungent penetrating odour and is strongly corrosive. It produces blisters on the skin. It is miscible with water, ethyl alcohol and ether in all proportions.

Chemical Properties. A little consideration of the structural formula of formic acid reveals that it has the structure of both an acid and an aldehyde.



Acid



Aldehyde

Hence formic acid combines the properties of an acid and an aldehyde. It considerably differs from other fatty acids in its chemical behavior.

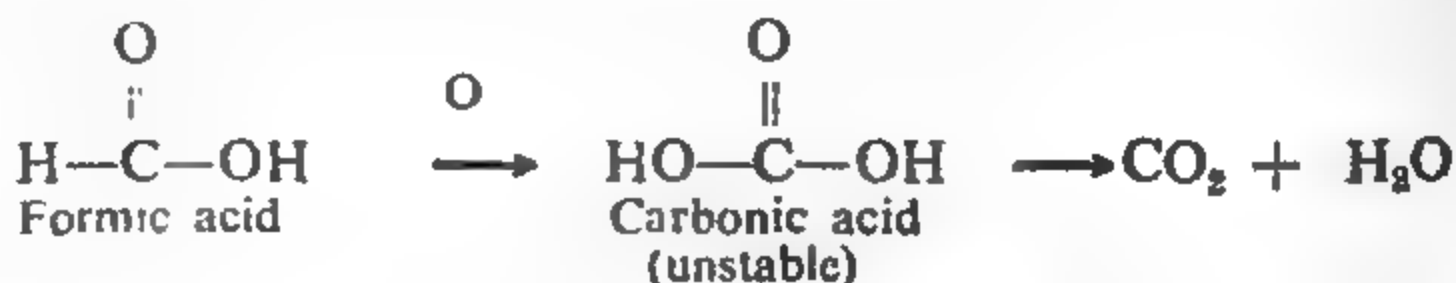
The reactions of formic acid can be discussed under two heads :

(a) *Reactions involving the lone H-atom.*

(b) *Reactions involving the —COOH group.*

(a) *Reactions involving the lone H-atom.*

(1) **Oxidation.** Formic acid can be readily oxidised by reagents like potassium permanganate, dichromate, silver oxide, etc., to give carbon dioxide and water.



(2) **Reducing properties.** Since formic acid can be readily oxidised it acts as a strong reducing agent. Like aldehydes, it reduces Fehlin's solution and ammoniacal solution of silver nitrate (cf. properties of aldehydes).



It also reduces potassium permanganate, potassium dichromate, mercuric chloride and other oxidising agents.



Mercuric
chloride

Formic acid

Mercurous
chloride

(3) **Decomposition of alkali salts.** Sodium or potassium formate when heated to about 360° , decomposes to give hydrogen and alkali oxalate.



Heat



+



Sodium formate

Sodium oxalate

(b) Reactions involving the $-\text{COOH}$ Group

(1) **Formation of salts.** Formic acid is much stronger than acetic acid or any other fatty acid. It readily forms water soluble salts, in the usual manner.



Formic acid

Sodium formate

(2) **Formation of esters.** Formic acid, on simple heating with alcohols, forms esters.

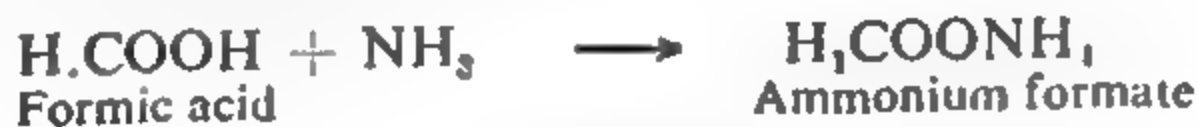


Formic acid

Ethyl alcohol

Ethyl formate

(3) **Formation of amides.** Formic acid combines with ammonia forming ammonium formate which on heating yields formamide with the loss of one molecule of water.



Formic acid

Ammonium formate

Heat



Ammonium formate



Formamide

(4) **Reaction with phosphorus pentachloride.** Formic acid is readily attacked by phosphorus pentachloride giving formyl chloride which being unstable decomposes to give hydrogen chloride and carbon monoxide.



Formic acid

Formyl chloride



Formyl chloride



(5) **Formation of aldehydes:** Calcium formate when heated alone gives formaldehyde.



When heated with calcium salt of another fatty acid, it yields other aldehydes. For example,



(6) **Decomposition reactions.** (i) Sodium formate when heated with soda lime yields hydrogen.



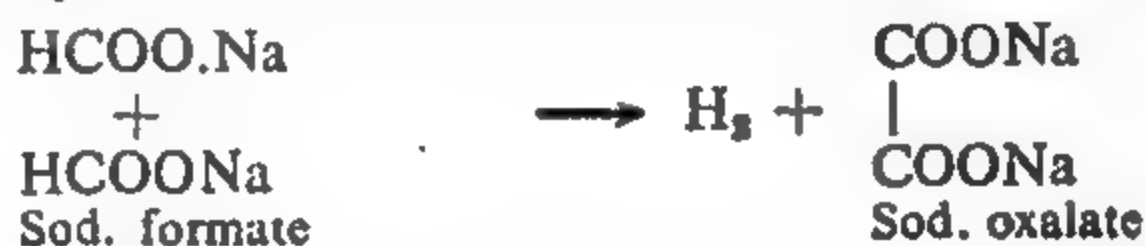
(ii) Formic acid, when heated alone at 160° , under pressure, decomposes into carbon dioxide and hydrogen.



(iii) In the presence of sulphuric acid, formic acid is dehydrated to carbon monoxide.



(iv) Sodium formate, when heated, decomposes to give sodium oxalate, as already mentioned.



Uses. 1. Formic acid is used for the preparation of mordants required in dyeing industry.

2. It is used in leather industry for the dehairing of hides.

3. Formic acid is also used in electroplating ; the presence of formic acid in the electrolytic bath gives a proper deposit of the metals.

4. Because of its antiseptic properties, formic acid is used in the preservation of fruit juices, etc., and also in the brewing industry.

5. It is also used in medicine as a remedy for gout and neuritis.

Tests. Formic acid can be detected by the following tests :

1. It has a characteristic pungent odour.

2. On warming with ethyl alcohol, a fruity smell of ethyl formate is obtained.

3. On warming with sodium bisulphite and adding sodium nitroprusside, a greenish blue colour is obtained.

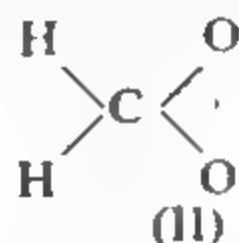
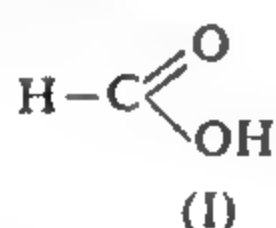
4. It reduces Fehling solution to red cuprous oxide and reduces ammoniacal silver nitrate to metallic silver.

5. On warming with mercuric chloride, a white precipitate of mercurous chloride is obtained which turns black on further heating due to the formation of mercury.

Tests No. 3, 4 and 5 are not given by acetic acid or any other fatty acid.

Structure. 1. The qualitative and quantitative analyses show that the molecular formula of formic acid is CH_2O_2 .

2. Keeping in view the tetravalency of carbon, bivalency of oxygen and univalency of hydrogen, two structures can be assigned to formic acid, viz.,

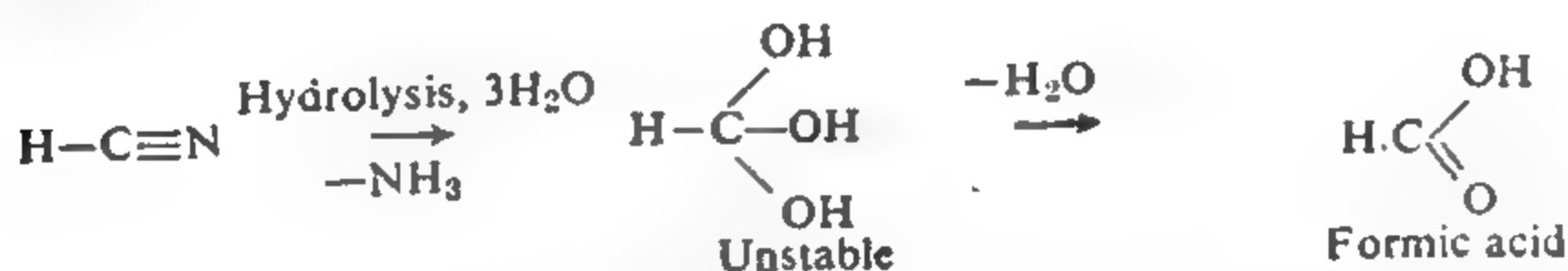


3. On treatment with sodium metal, hydrogen is evolved. Also with phosphorus pentachloride hydrogen chloride gas is given out. Both these reactions indicate the presence of a hydroxyl group in formic acid.

This rules out structure (II) and supports structure (I).

4. Structure (I) also contains the aldehyde group and thus accounts for the reducing properties of formic acid.

5. The structure of formic acid is confirmed by its synthesis from hydrogen cyanide.



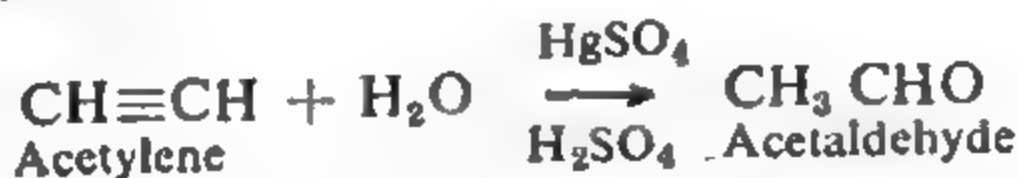
ACETIC ACID, ETHANOIC ACID, CH_3COOH

It is the earliest known fatty acid. It is the chief constituent of vinegar and hence its name (Latin. *acetum* means vinegar). Dilute acetic acid, in the form of vinegar was, in fact, the only acid known to ancients.

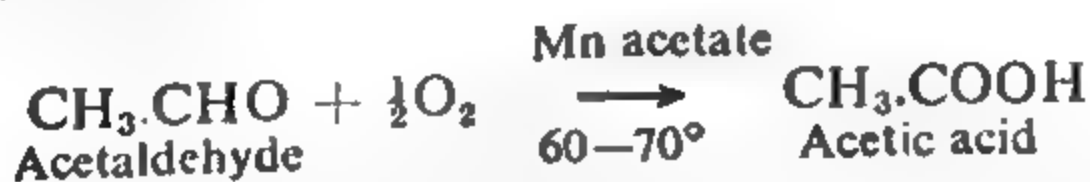
Industrial Preparation. Acetic acid is prepared on an industrial scale by the following methods :

(1) **From acetylene.** The most economical method for the production of pure acetic acid or glacial acetic acid is from acetylene.

Acetylene, obtained from calcium carbide is passed into an aqueous solution of sulphuric acid containing mercuric sulphate when acetaldehyde is formed.

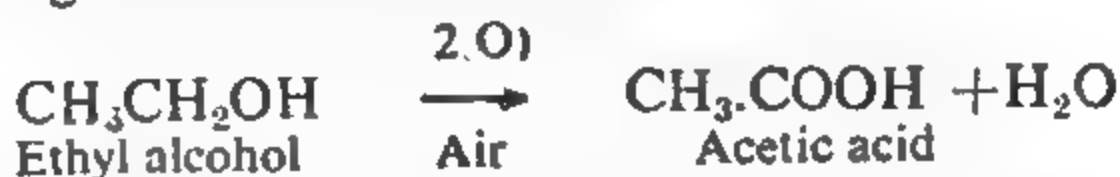


The vapour of acetaldehyde are mixed with air and the mixture passed over manganese acetate (catalyst) at $60-70^\circ$, when acetaldehyde is oxidised to acetic acid.



(2) **From ethyl alcohol.** Large amounts of acetic acid are prepared these days by the catalytic oxidation of ethyl alcohol. Ethyl alcohol vapour are mixed with air and passed over a heated metal catalyst when ethyl alcohol gets oxidised to acetic acid.

(3) **Fermentation process.** The oldest method for the preparation of acetic acid involves the fermentation of ethyl alcohol in dilute solution, in contact with air, under the influence of the bacteria *mycoderma aceti* when ethyl alcohol gets oxidised to acetic acid.



These days, the fermentation is carried out by the **Quick Vinegar process**, described below :

A large number of wooden vats, filled with wooden shavings or twigs, are arranged in series. One such vat is shown in Fig. 2. It has a perforated false bottom and a perforated top. It is also provided with air inlets near the base as shown.

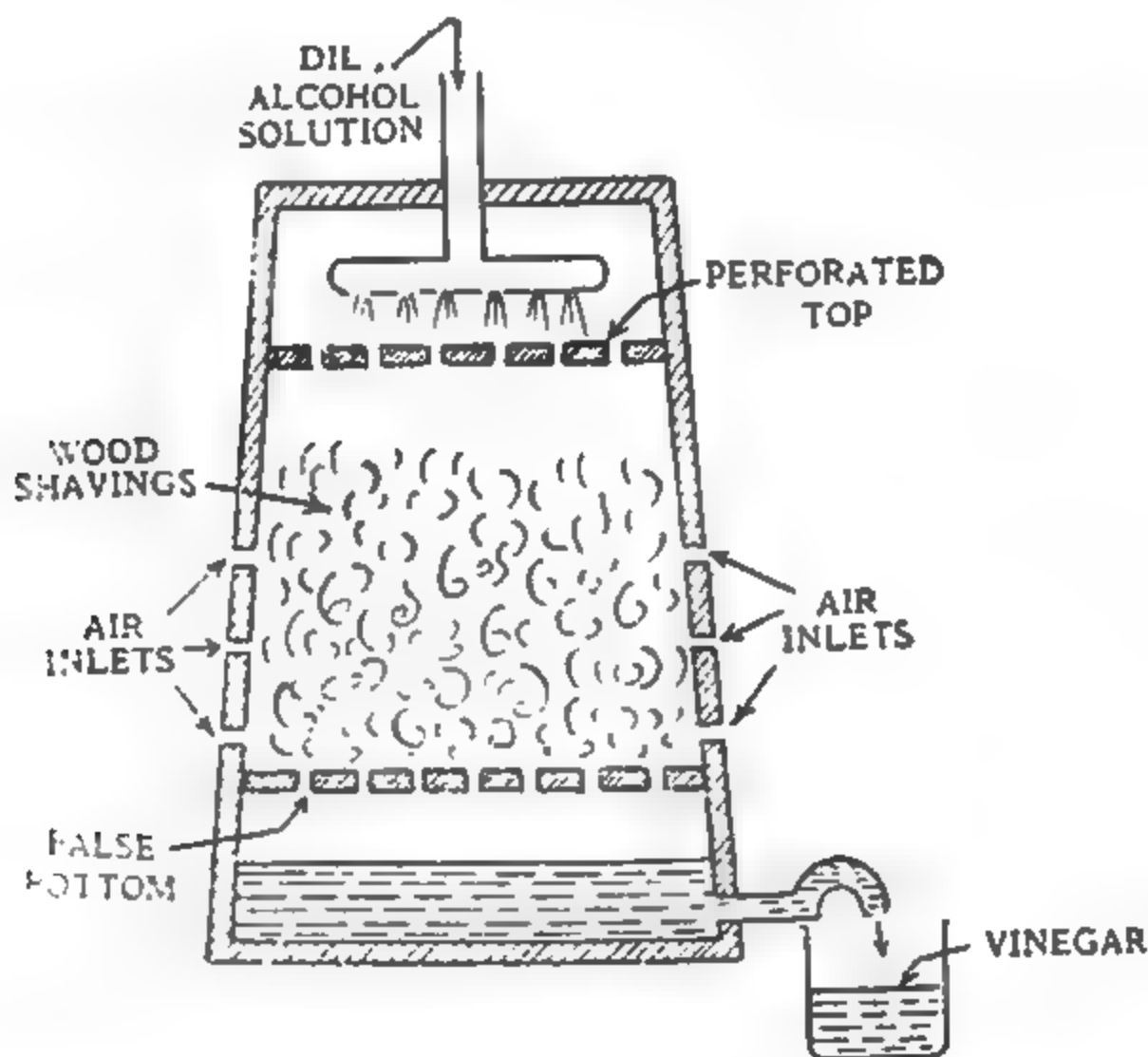


Fig. 2. Manufacture of Vinegar.

The wood shavings are impregnated with strong vinegar which supplies the acetous ferment. Dilute alcohol solution is then allowed to trickle down from the top. Air is drawn in through the air inlets and moves upwards. The alcohol is oxidised to acetic acid. The heat generated in the oxidation process maintains the temperature at about 35° which is the optimum temperature for the proper development and activity of the bacteria. The supply of air is carefully controlled. If the air admitted is too much, the alcohol may be oxidised to carbon dioxide and water and if it is too less the alcohol may be oxidised only to acetaldehyde.

The liquor obtained from first vat is introduced at the top of the second vat and so on. This recirculation process results in the production of about 10 per cent acetic acid solution.

The vinegar obtained above is then subjected to careful fractionation to obtain pure acetic acid. It is only recently that vinegar has been used for the production of acetic acid on a commercial scale. This has been possible entirely due to the development of highly efficient methods of fractionation.

(4) **From wood distillation.** Another method for the production of acetic acid is from wood distillation (see page 354).

Properties. Acetic acid is a colourless corrosive liquid (b.p. 118°) with a pungent smell, miscible with water, alcohol and ether in all

proportions. When sufficiently cooled it forms ice-like crystals (m.p. 16.6°) and hence the name **glacial acetic acid**. It is a good solvent for sulphur, iodine and many organic substances.

Chemically, it gives all the reactions of fatty acids (see general properties of fatty acids).

Uses. Acetic acid is commonly used as a solvent and for the manufacture of acetates, acetone, esters, etc. Cellulose acetate, required for making photographic films and rayon, is obtained by dissolving cellulose in glacial acetic acid. Its esters, ethyl acetate and amyl acetate, are used as excellent industrial solvents.

2. In the form of vinegar, acetic acid is commonly used as a condiment for preparing pickles. It is also employed for curing meat and fish.

3. In the laboratory, it is used as a reagent and also as a solvent for many reactions because it is not attacked by oxidising and reducing agents.

4. It is also used in medicine.

Tests. Acetic acid can be identified by the following tests:

1. It has a characteristic pungent smell.

2. When heated with alcohol in the presence of sulphuric acid, a fruity smell of ethyl acetate is obtained.

3. *Ferric chloride test.* A small amount of the acid is neutralised with ammonia or sodium hydroxide and ferric chloride solution is added. A blood red colour is obtained. Boil the solution, the red colour is replaced by a brown precipitate.

Formic acid also gives this test.

4. *Cacodyl test.* A small amount of the acid is neutralised with potassium hydroxide and the solution is evaporated to dryness. The residue is heated with a small amount of arsenious oxide. An extremely nauseating smell of cacodyl oxide is obtained.

This test is not given by formic acid.

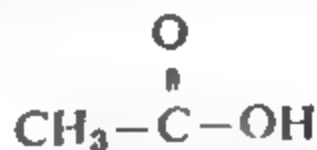
Structure. (1) The qualitative and quantitative analyses show that the molecular formula of acetic acid is $C_2H_4O_2$

(2) Prolonged treatment of boiling acetic acid with chlorine yields trichloroacetic acid, $C_2HO_2Cl_3$, showing, thereby, that of the four hydrogen atoms in the acetic acid molecule, three have been replaced by chlorine. This suggests the presence of a methyl group in acetic acid.

(3) On treatment with phosphorus pentachloride, acetic acid gives acetyl chloride, and hydrogen chloride is evolved. This indicates the presence of a hydroxyl group.

Thus, acetic acid contains a methyl group and a hydroxyl group.

(4) Keeping in view the valency requirements of carbon, oxygen and hydrogen, only one structural formula is possible for acetic acid, viz.,



(5) Oxidation of acetaldehyde to acetic acid supports the above structure:



Distinction between Formic acid and Acetic acid

(For equations of reactions refer to previous pages).

(1) **Oxidation.** Formic acid is readily oxidised to CO_2 and H_2O . Acetic acid is not oxidised.

(2) **Reducing properties.** Formic acid reduces Fehling solution, ammoniacal solution of AgNO_3 , potassium permanganate, mercuric chloride, etc.

Acetic acid does not behave as a reducing agent.

(3) **Decomposition reactions.** Formic acid gives a variety of decomposition reactions. For example, when heated alone at 160° under pressure it decomposes into CO_2 and H_2 ; when heated with H_2SO_4 it gives CO . Its sodium salt decomposes, on heating, to give H_2 and sodium oxalate.

Acetic acid does not give such type of decomposition reactions.

(4) **Heating calcium salt.** Calcium formate on heating gives formaldehyde, whereas calcium acetate gives acetone.

(5) **Heating sodium salt with soda lime.** Sodium formate on heating with sodalime gives hydrogen, whereas sodium acetate gives methane.

(6) **Formation of anhydride.** Acetic acid, on heating with P_2O_5 , readily gives acetic anhydride. Formic acid does not give formic anhydride. It loses water to give carbon monoxide.

(7) **Special tests** (i) Formic acid, on warming with NaHSO_3 and adding sodium nitroprusside gives a green blue colour.

Acetic acid does not give this test.

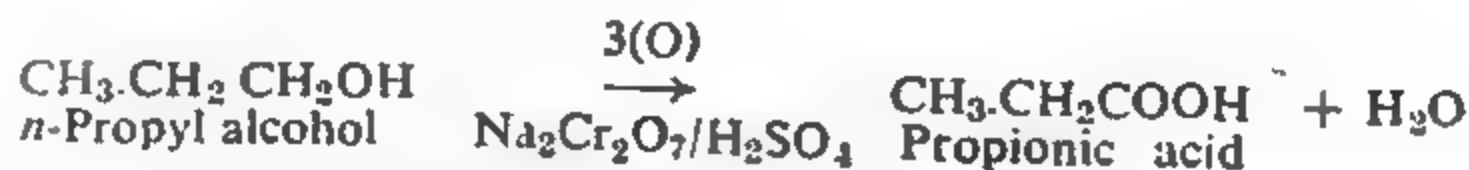
(iii) Acetic acid, when neutralised with KOH , evaporated to dryness and then heated with arsenious oxide, gives an extremely nauseating smell of cacodyl oxide (*cacodyl test*).

Formic acid does not give this test.

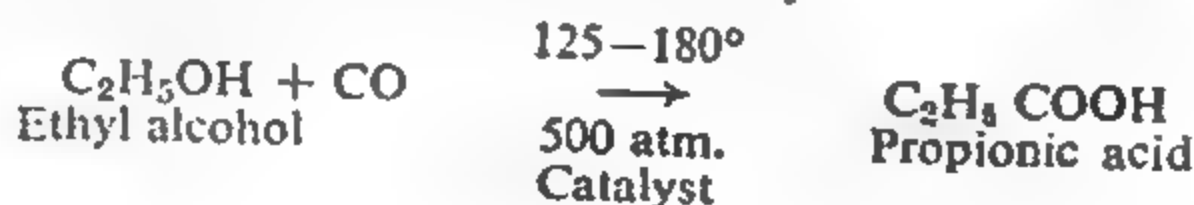
Propionic acid, $\text{C}_2\text{H}_5\text{COOH}$

Preparation. Propionic acid is prepared on a large scale :

(1) By the oxidation of *n*-propyl alcohol.



(ii) By heating carbon monoxide and ethyl alcohol at $125-180^\circ$ under pressure, in the presence of a catalyst (boron trifluoride).



Properties. Propionic acid is a colourless liquid, boiling at 141° . It is miscible with water, ethyl alcohol and ether in all proportions. Chemically, it resembles acetic acid.

Butyric acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$

It occurs in butter as glyceryl ester. The foul smell of rancid butter is due to the liberation of free butyric acid as a result of the decomposition of the glyceryl ester by hydrolysis or oxidation. Butyric acid is also present in perspiration.

Butyric acid is a viscous, unpleasant smelling liquid, boiling at 162° . It is miscible with water, ethyl alcohol and ether. It gives the usual reactions of fatty acids.

Higher Fatty Acids.

Of the higher fatty acids, the most important are palmitic acid, $\text{C}_{15}\text{H}_{31}\text{COOH}$ and stearic acid $\text{C}_{17}\text{H}_{35}\text{COOH}$. They occur in the form of glyceryl esters in all vegetable oils and fats from which they can be obtained by hydrolysis with steam under pressure.

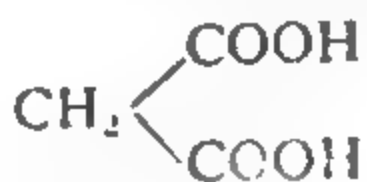
Palmitic acid and stearic acid are colourless, waxy solids, melting at 62° and 69° respectively. They are insoluble in water but are readily soluble in alcohol and ether. The acids are used in candle industry. Their sodium salts are soaps.

DICARBOXYLIC ACIDS

Dicarboxylic acids, as the name suggests, are compounds containing two carboxylic (COOH) groups in their molecule. They are generally known by their common names. For example,



Oxalic acid



Malonic acid



Succinic acid

The I.U.C. names are obtained by using the suffix, *dioic* as for example,

$\text{HOOC}\cdot\text{COOH}$ is ethanedioic acid,

$\text{HOOC}\cdot\text{CH}_2\cdot\text{COOH}$ is propanedioic acid,

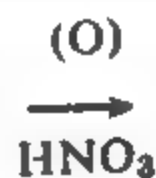
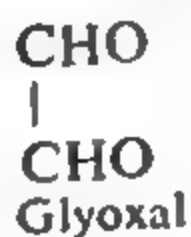
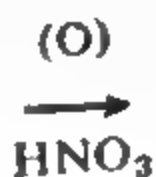
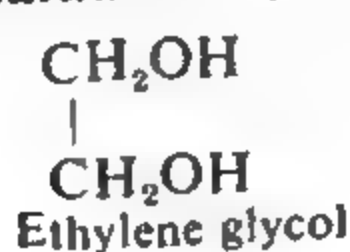
and $\text{HOOC}(\text{CH}_2)_2\cdot\text{COOH}$ is butanedioic acid.

The important members of the series are oxalic acid, malonic acid and succinic acid.

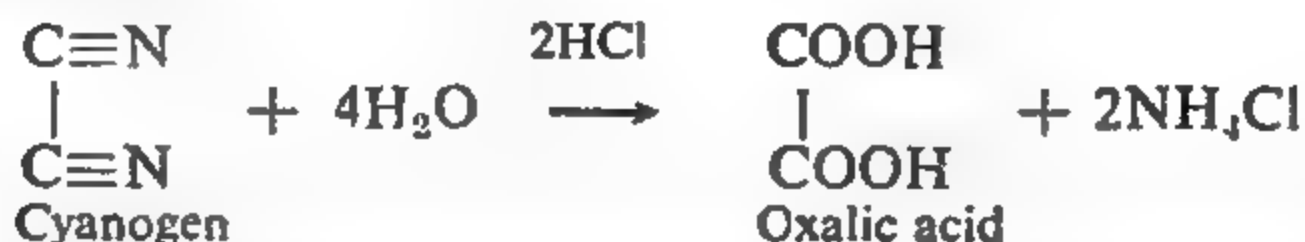
OXALIC ACID, $\text{HOOC}\cdot\text{COOH}$

Oxalic acid is widely distributed in the vegetable kingdom in the form of potassium hydrogen oxalate. It occurs in rhubarb, tobacco, in sorrel and other plants of the *oxalis* group. The name of the acid is also derived from the word *oxalis*.

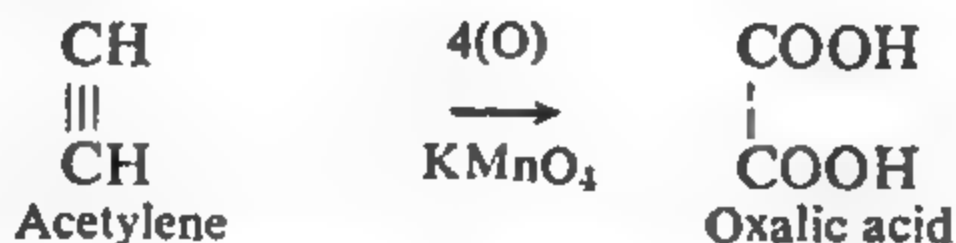
Preparation. (1) By the oxidation of ethylene glycol with nitric acid.



(2) By the hydrolysis of cyanogen in the presence of concentrated hydrochloric acid.



(3) By the oxidation of acetylene with hot acidic or alkaline permanganate.



(4) By heating sodium in a current of carbon dioxide at 360°



The free acid is obtained from the sodium salt as described in the commercial method below.

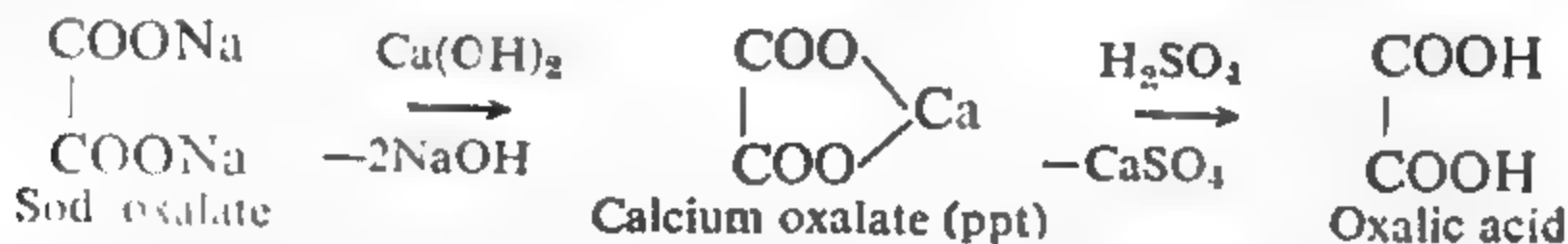
(5) Commercial Method. By heating sodium formate rapidly at 360° .



Sodium formate is obtained by passing carbon monoxide in sodium hydroxide under pressure (see page 424).

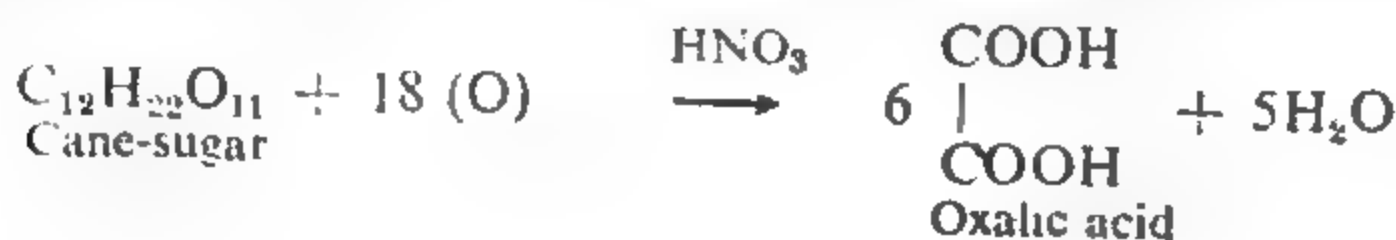


The sodium oxalate obtained above is dissolved in water and treated with lime when a precipitate of calcium oxalate is obtained. This precipitate is separated by filtration and treated with a calculated amount of sulphuric acid. The precipitated calcium sulphate is removed by filtration and the solution of oxalic acid left is evaporated to get the crystals of the acid.



Previously, oxalic acid was manufactured from saw dust by heating the latter with sodium and potassium hydroxides in iron pans at $200\text{--}220^\circ$ in air. The alkali oxalate first formed was extracted with water and treated as above for the liberation of the free acid. This method is now almost obsolete.

(6) Laboratory preparation. Oxalic acid is conveniently prepared in the laboratory by the oxidation of cane sugar with concentrated nitric acid.



150 ml. of concentrated nitric acid is taken in a large flask and 50 gm. of coarsely powdered cane-sugar added to it. The flask is heated on a water bath, for some time, in a fume closet, till the reaction starts with the evolution of copious fumes of nitrogen peroxide. Heating is then stopped and the reaction allowed to proceed as such till the evolution of brown fumes ceases. The contents of the flask are transferred to a china dish and concentrated to get crystals of oxalic acid ($C_2H_2O_4 \cdot 2H_2O$).

The acid may be further purified by recrystallisation.

Physical Properties. Oxalic acid is a crystalline solid with two molecules of water of crystallisation. It is freely soluble in water and alcohol but only sparingly soluble in ether. It is poisonous.

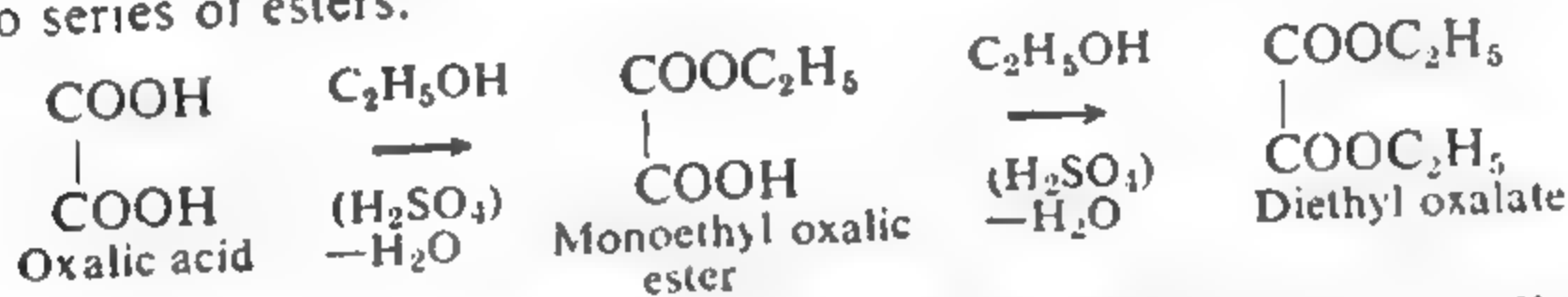
The crystalline acid melts at 101.5° and the anhydrous acid at 189.5° .

Chemical Properties. Oxalic acid gives all the reactions of carboxylic acids. One or both the carboxyl groups may enter into chemical reaction at a time. The important reactions are :

(1) Oxalic acid reacts with **alkalies** forming two series of salts.



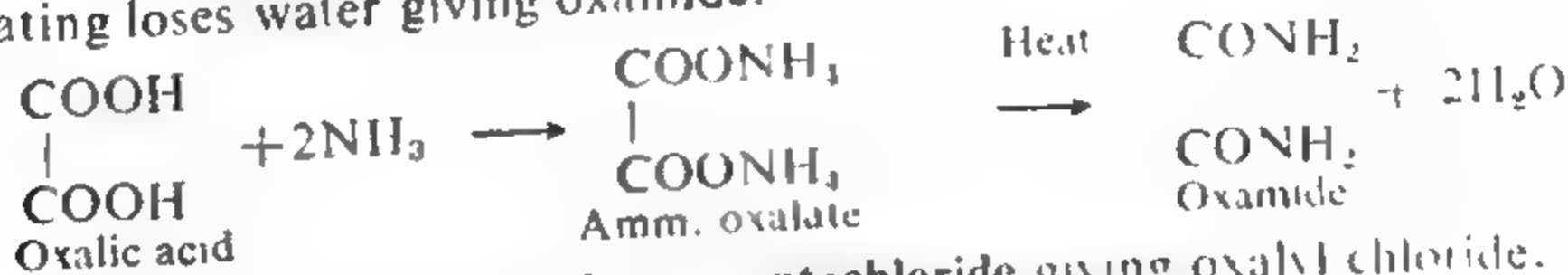
(2) It reacts with **alcohols** in the presence of sulphuric acid giving two series of esters.



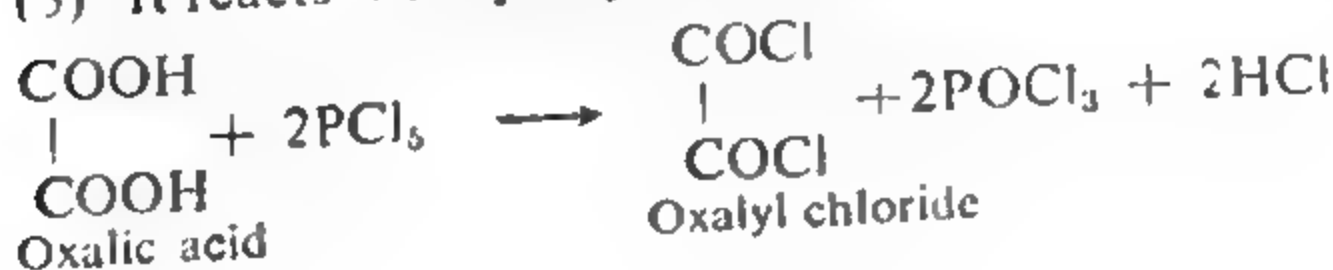
(3) It decomposes **carbonates** and **bicarbonates** giving carbon dioxide.



(4) It reacts with **ammonia** giving ammonium oxalate which on heating loses water giving oxamide.

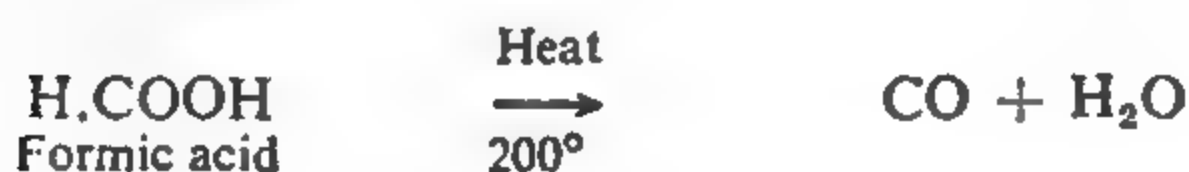
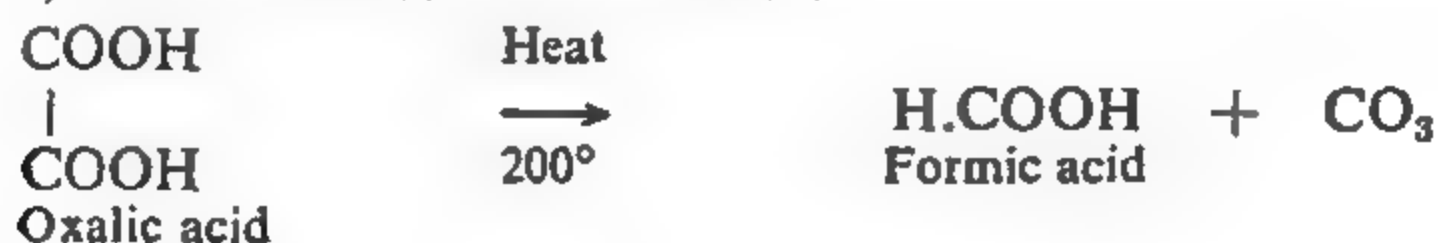


(5) It reacts with **phosphorus pentachloride** giving oxalyl chloride.



(6) Oxalic acid, when heated at $100-105^{\circ}$, loses water of crystallisation, giving the anhydrous acid.

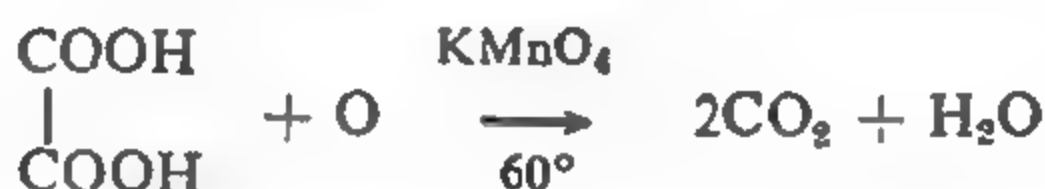
On heating at about 200° , it decomposes into carbon dioxide, formic acid, carbon monoxide and water.



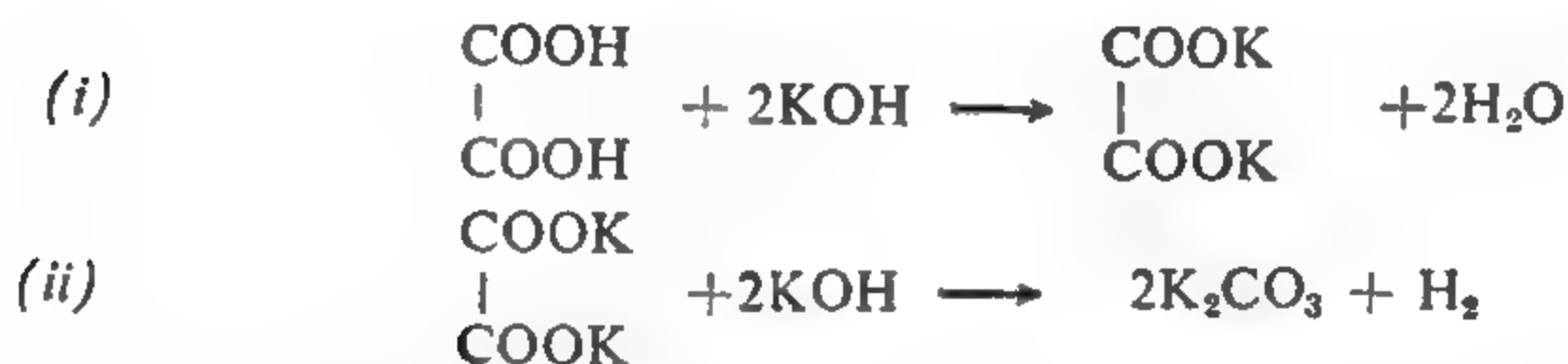
(7) Oxalic acid is easily decomposed into carbon monoxide, carbon dioxide and water on heating with concentrated sulphuric acid at 90° .



(8) Oxalic acid is readily oxidised to carbon dioxide by hot acidic permanganate.

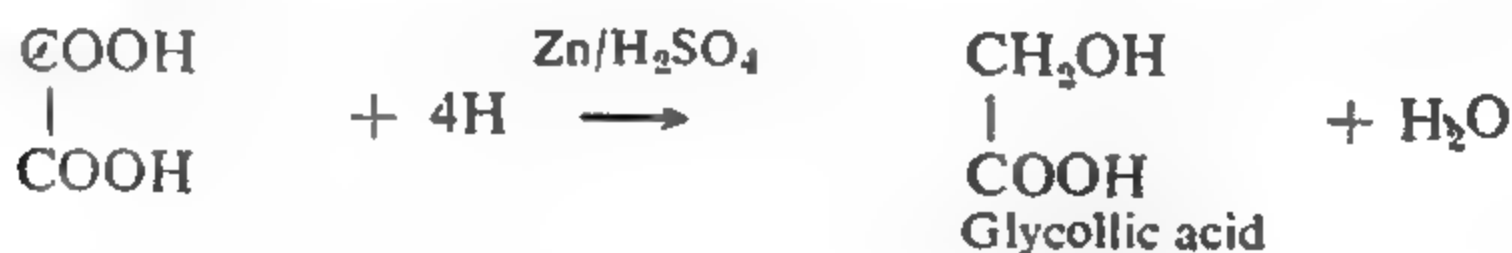


(9) When fused with potassium hydroxide oxalic acid gives hydrogen.



(10) When heated with glycerol at 120° , oxalic acid gives formic acid and on heating at 260° , allyl alcohol is formed (see reactions of glycerol).

(11) When reduced with zinc and sulphuric acid, oxalic acid forms glycollic acid.



Uses. Oxalic acid is used :

(i) For the manufacture of ink (ii) For bleaching straw (iii) For making metal polishes (iv) For the preparation of formic acid

and allyl alcohol (v) Its antimony salts are used as mordants in dyeing and printing (vi) As a reagent in volumetric analysis.

Tests Oxalic acid may be identified by the following tests :

(1) On heating with concentrated sulphuric acid, it gives CO_2 and CO , the latter burns with a bluish flame.

(2) It decolorises acidified potassium permanganate, on warming, with the evolution of carbon dioxide.

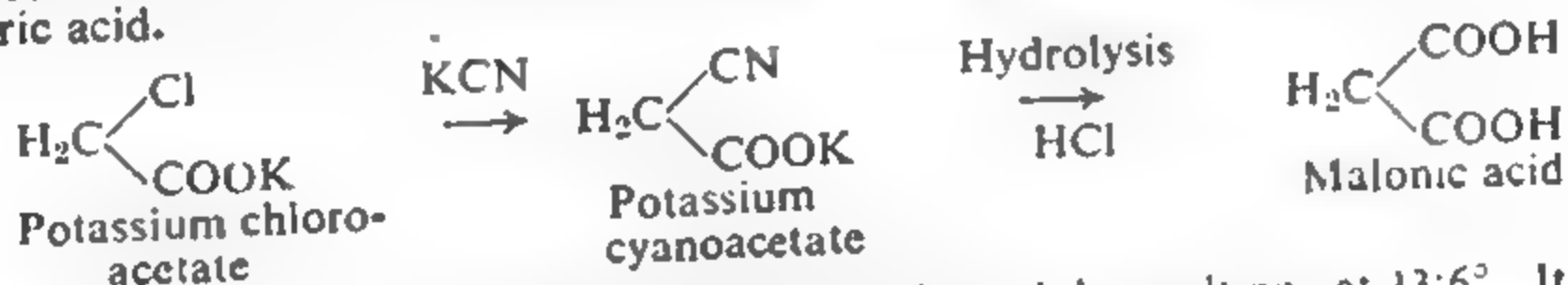
(3) On adding silver nitrate or calcium chloride to neutral solution of oxalic acid, a white precipitate is formed.

(4) With ferrous sulphate, a yellow precipitate of ferrous oxalate is obtained.

MALONIC ACID, $\text{CH}_2(\text{COOH})_2$

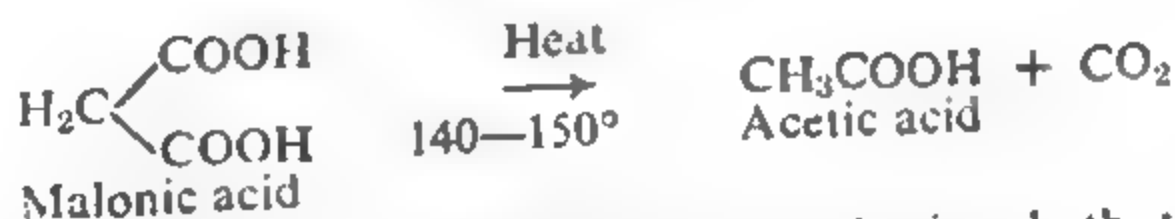
Malonic acid occurs in sugar beets in the form of its calcium salt.

Preparation. Malonic acid is prepared by heating potassium chloroacetate with aqueous potassium cyanide and hydrolysing the potassium cyanoacetate formed with hydrochloric acid.



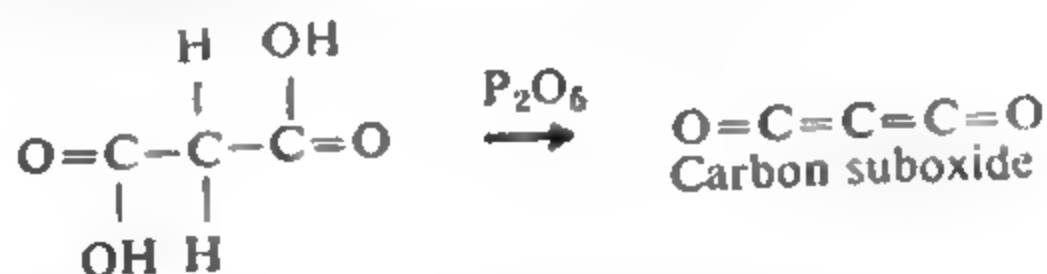
Properties. Malonic acid is a colourless, crystalline solid, melting at 13.6° . It is soluble in water and alcohol but sparingly soluble in ether.

On heating to $140-150^\circ$, it readily loses a molecule of carbon dioxide giving acetic acid.



It may be remembered that all dicarboxylic acids, having both the carboxylic groups attached to the same carbon atom, readily lose a molecule of carbon dioxide on heating, yielding monocarboxylic acids.

When heated with phosphorus pentoxide, malonic acid loses two molecules of water to form carbon suboxide.



Malonic acid gives all the reactions of a dicarboxylic acid.

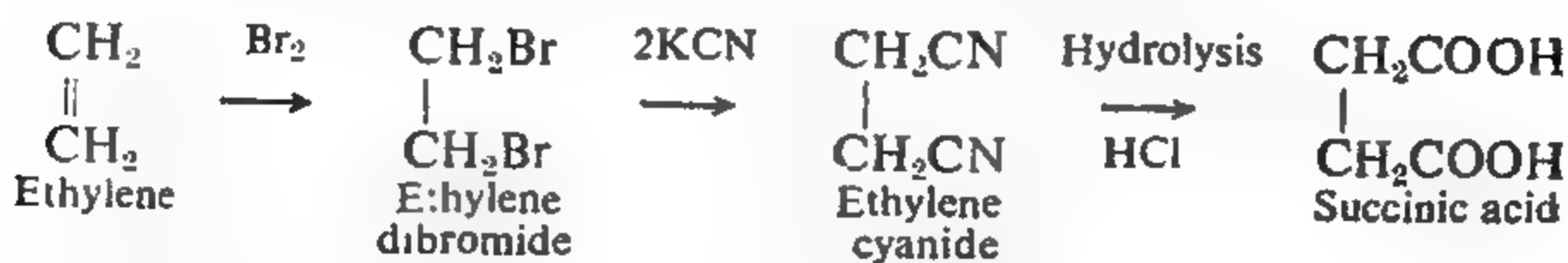
From synthetic point of view, the malonic esters are much more important than the acid itself.

SUCCINIC ACID, $(\text{CH}_2\text{COOH})_2$

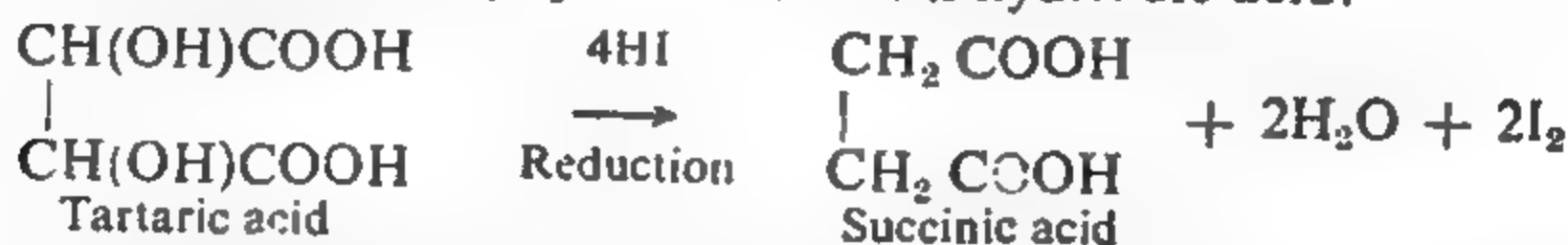
Succinic acid was originally obtained by the distillation of amber and hence the name (Latin. *succinum*=amber). It is also formed in small amounts during the fermentation of sugar and other substances. It also occurs in unripe fruits.

Preparation. Succinic acid may be obtained by the following methods :

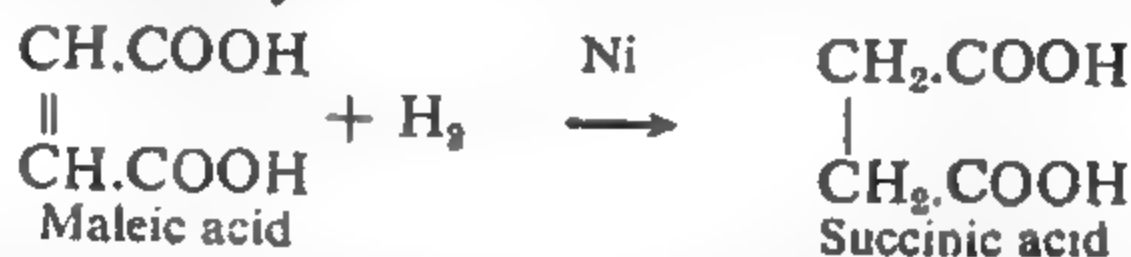
(1) From ethylene, through the reactions shown below :



(2) From tartaric acid, by reduction with hydriodic acid.



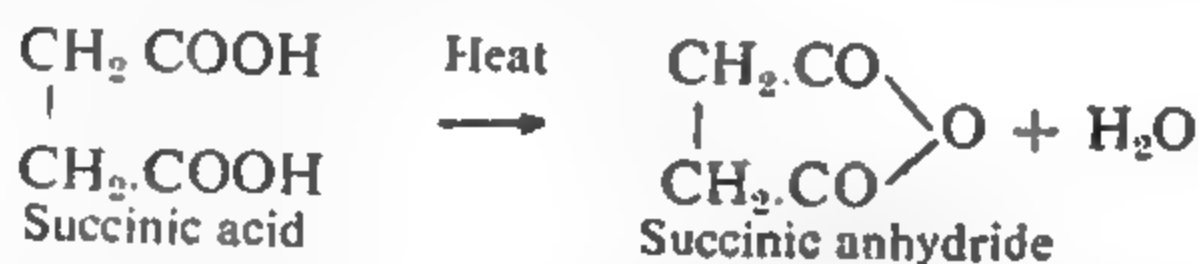
(3) From maleic acid, by reduction with hydrogen in the presence of nickel as a catalyst.



Properties. Succinic acid is a crystalline solid, melting at 185° . It is moderately soluble in water and ethyl alcohol but sparingly soluble in ether.

Chemically, it gives all the reactions characteristic of dicarboxylic acids.

When heated, most of the acid sublimes. The remaining portion is converted into the anhydride.



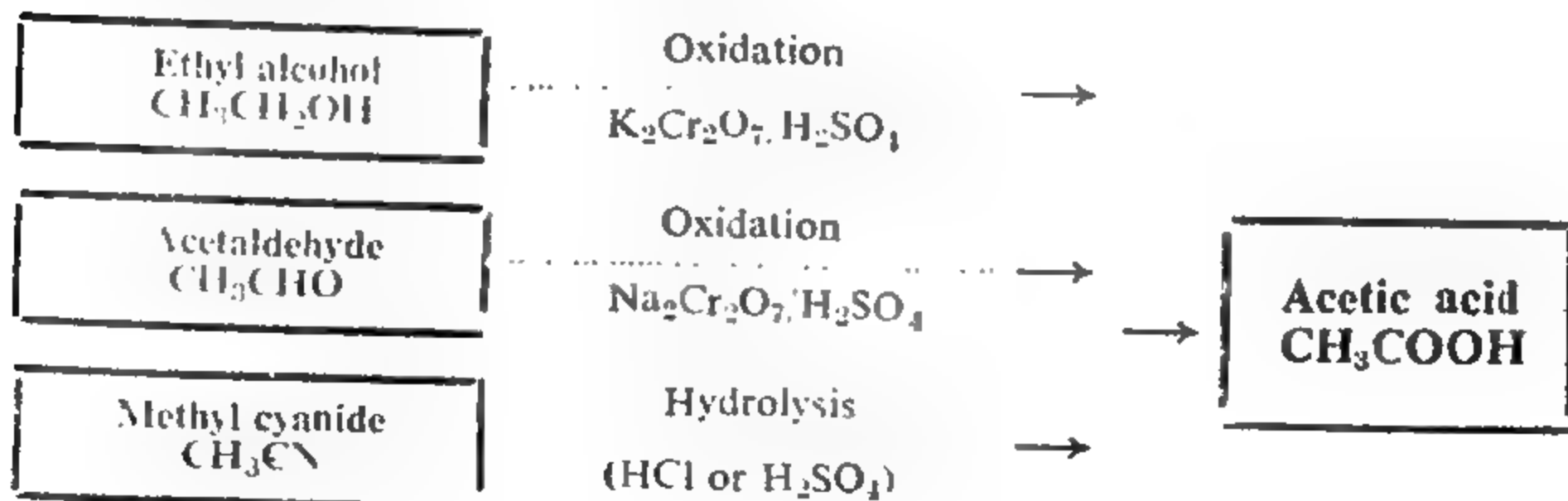
If potassium succinate is electrolysed, ethane is produced (see preparation of ethane).

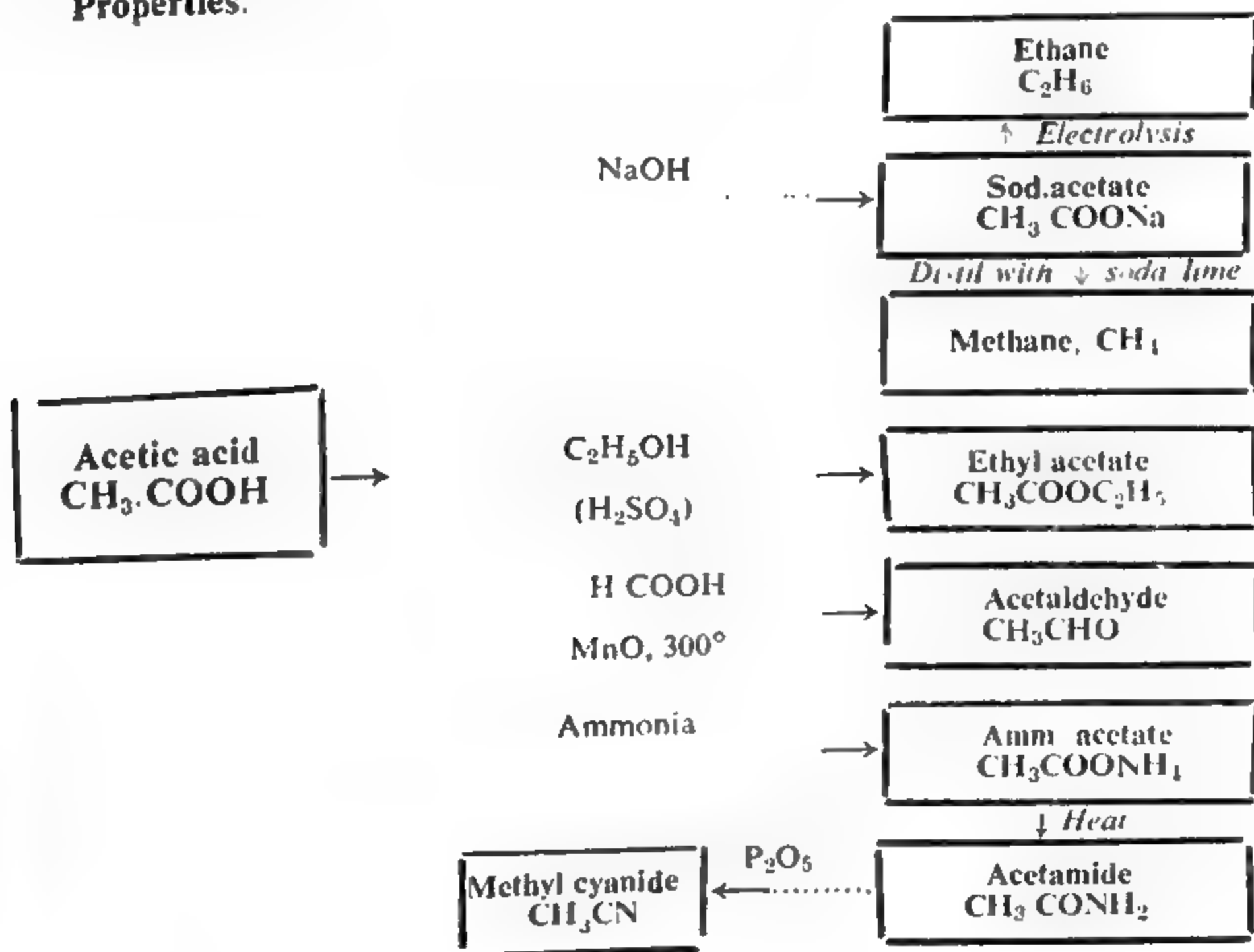
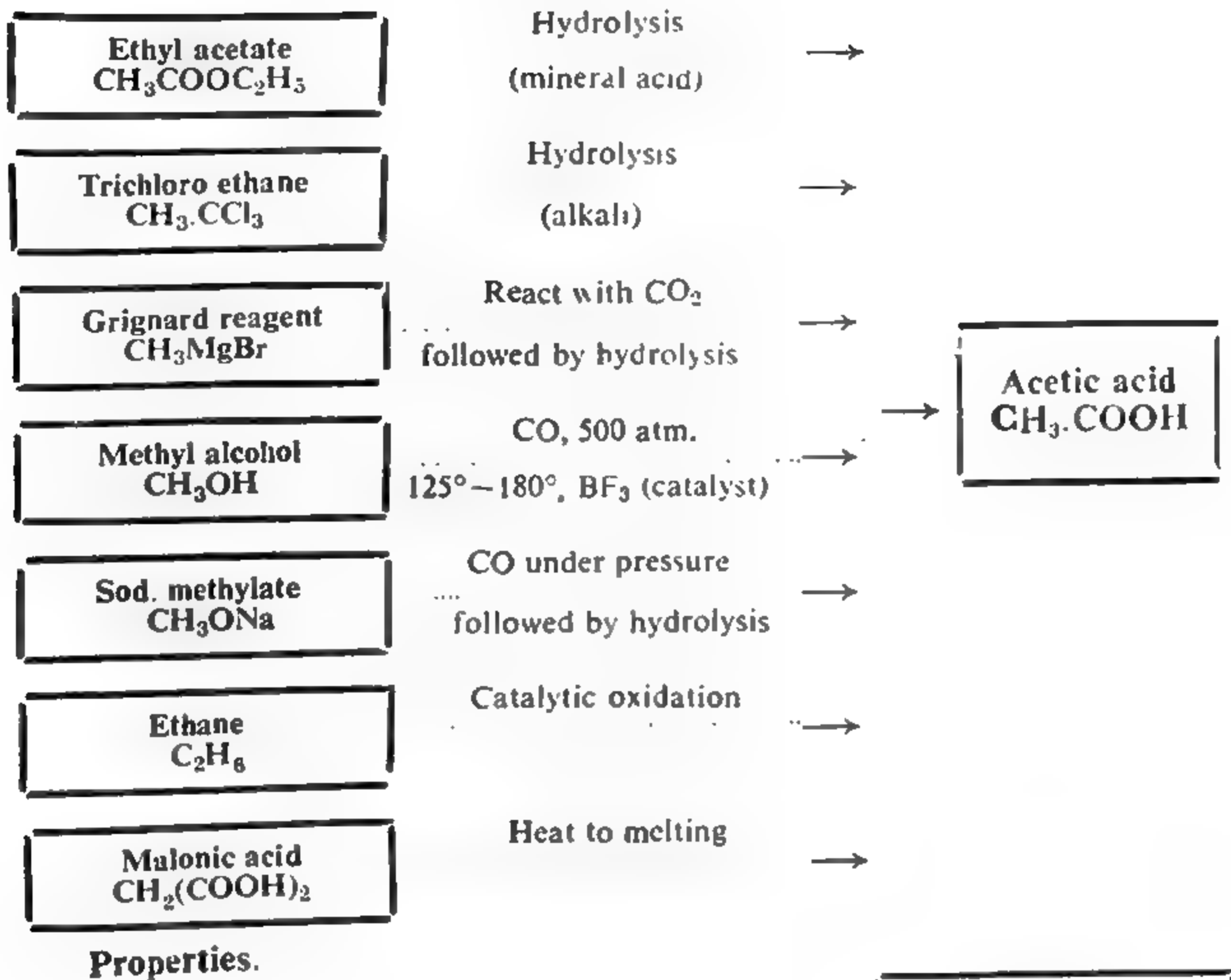
Succinic acid is used in the preparation of perfumes. It is also used in dyeing and medicine and in volumetric analysis.

SUMMARIES OF TYPICAL MEMBERS

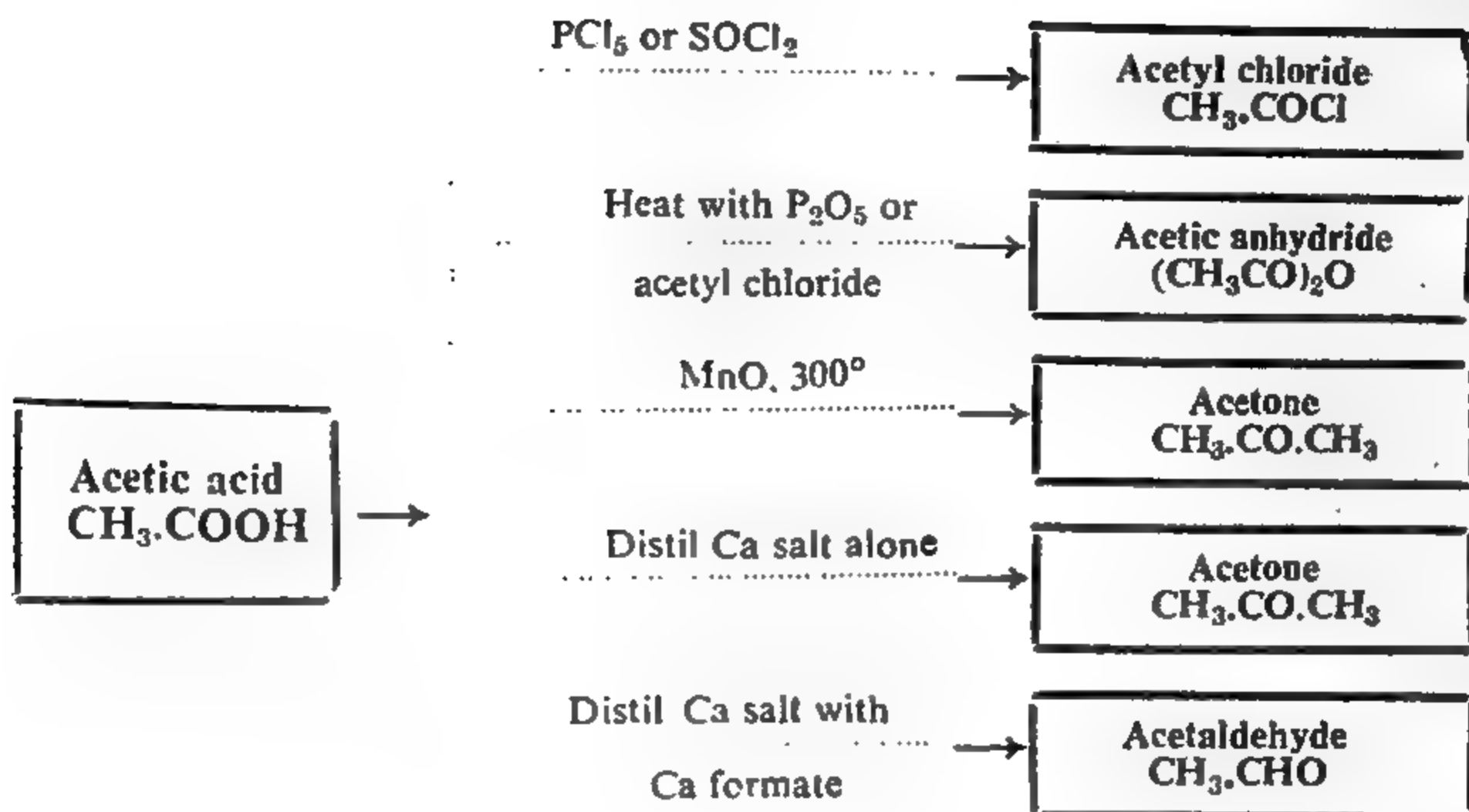
PREPARATION AND PROPERTIES OF ACETIC ACID

Preparation.



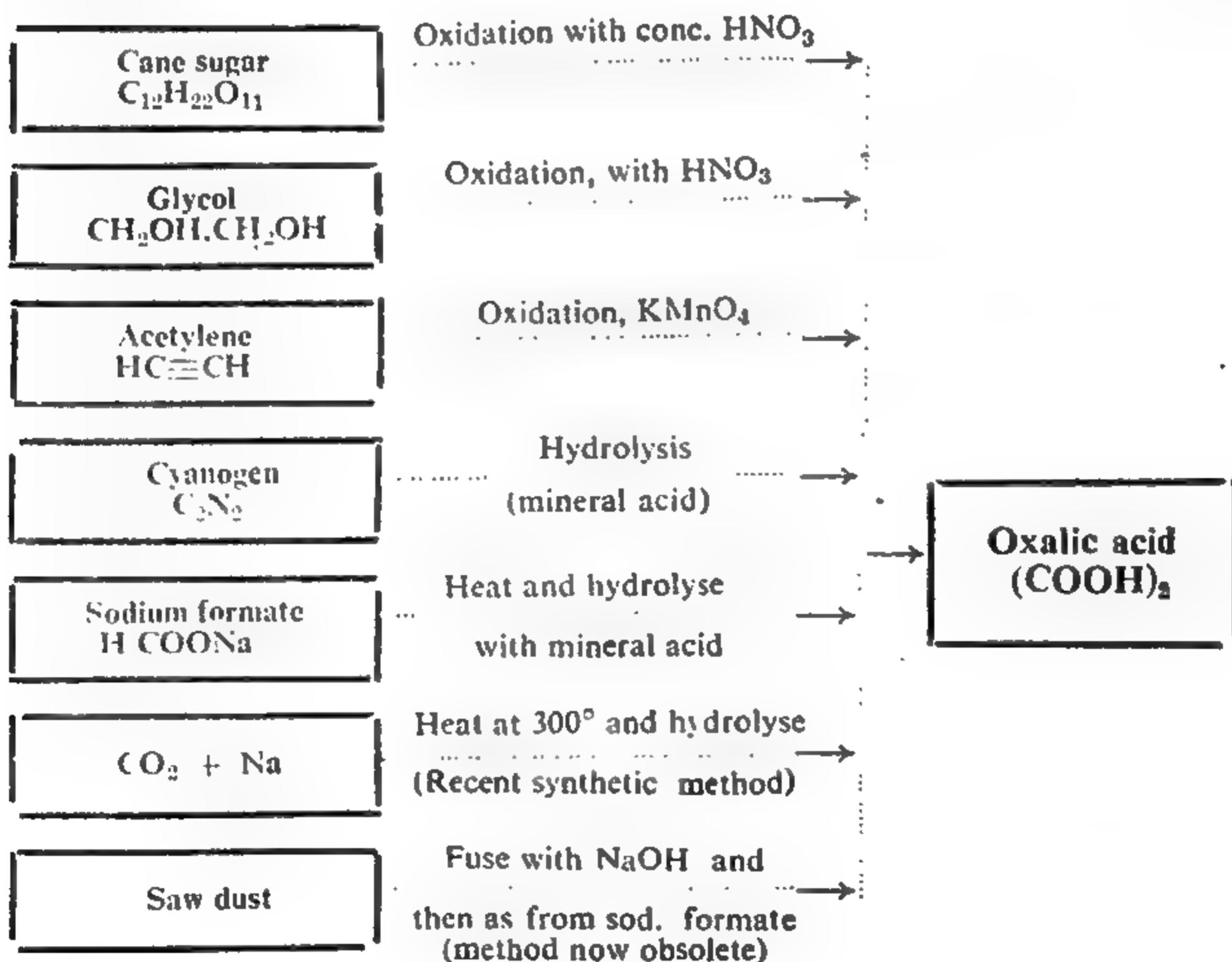


SUMMARIES

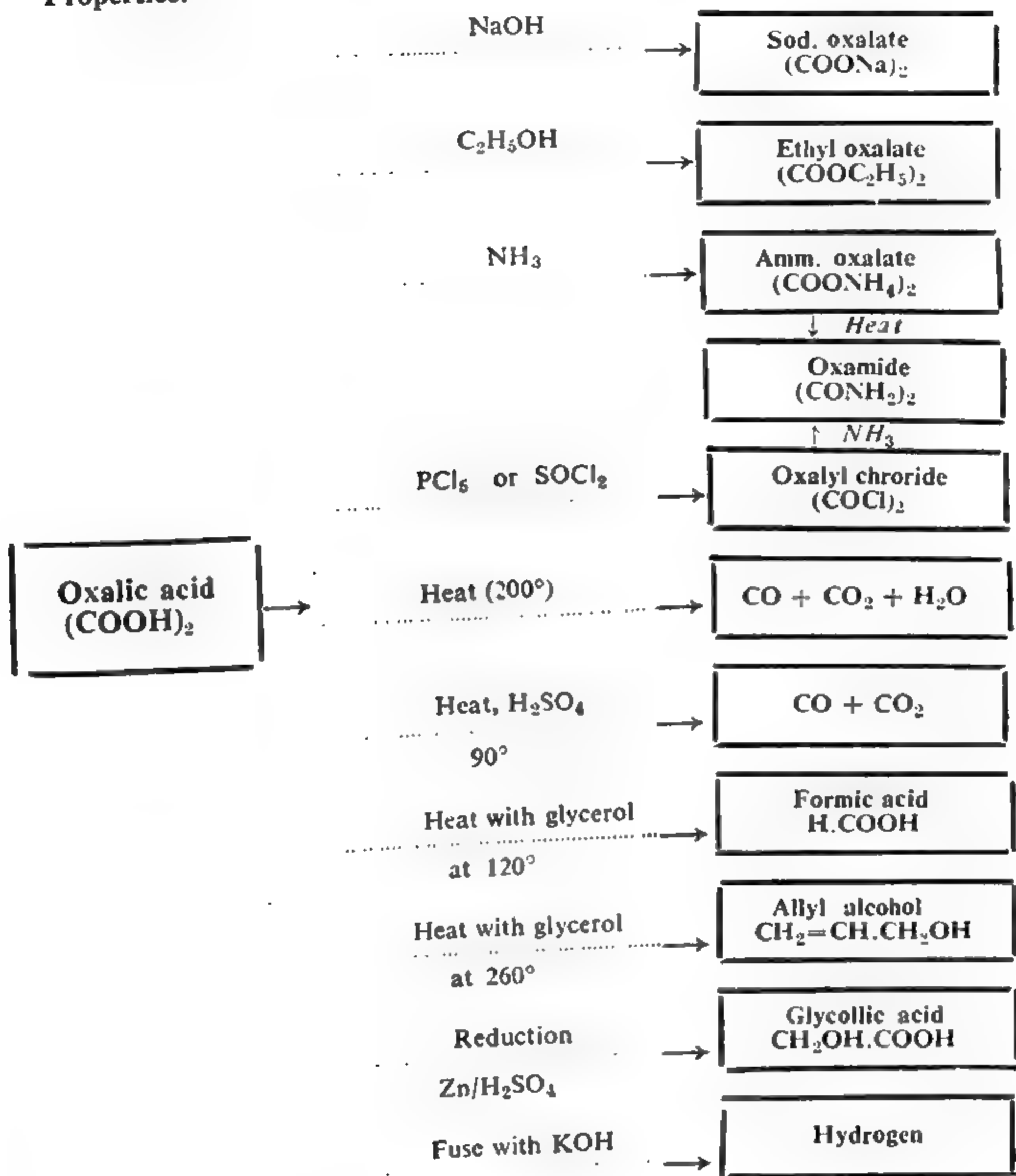


PREPARATION AND PROPERTIES OF OXALIC ACID

Preparation.



Properties.



QUESTIONS

1. What are fatty acids? Why are they so called?
2. Give the general methods of preparation and properties of mono-carboxylic acids.
3. How is anhydrous formic acid prepared in the laboratory? Show that it behaves both as an acid and an aldehyde. Describe its uses.

4. How is formic acid prepared industrially? Describe its important properties and uses. What tests would you apply to identify formic acid?
5. How is acetic acid prepared on a commercial scale? Describe its important uses
6. Compare and contrast the properties of acetic acid and formic acid. How do you account for the difference in their chemical behaviour?
7. How is formic acid prepared in the laboratory? How can it be converted into (i) Oxalic acid (ii) Methyl alcohol (iii) Formaldehyde (iv) Acetaldehyde?
8. How is acetic acid prepared? Explain how it can be converted into (i) Methane (ii) Ethane (iii) Acetone (iv) Acetaldehyde (v) Acetyl Chloride (vi) Acetamide?
9. Describe any three methods of preparation, four chemical properties and two uses of oxalic acid. (Panjab Inter 1959)
10. Devise a scheme for each of the following conversions :
(i) Oxalic acid into formic acid. (ii) Formic acid into oxalic acid. (Panjab Inter 1954)
11. Outline a scheme for preparing propionic acid starting from methyl alcohol. (Panjab Inter 1957)
12. Why are "fatty acids" so called? Give the names and structural formula of at least three of them which are not consecutive homologues. How does the first member of the series differ from the rest? (Panjab Inter 1952)
13. What is glacial acetic acid? How can you distinguish it from formic acid? (Panjab Inter 1950)
14. Convert formic acid into acetic acid and *vice versa*. How will you distinguish chemically acetic acid from formic acid? (Panjab Inter 1945)
15. How is succinic acid obtained synthetically and on a large scale? How can it be obtained from maleic and tartaric acids? What is the action of heat on succinic acid and ammonium succinate? (Panjab Inter 1948)
16. Starting from acetic acid how will you synthesise the following :—
(a) Methane (b) acetaldehyde (c) acetic anhydride (d) methylamine
(e) acetone. (Panjab T.D.C. Part I 1963)
17. Describe the method of preparation of oxalic acid from cane-sugar. Give synthetic methods of its preparation as well. What is the action of oxalic acid upon the following :—
(1) Heat (2) NH_3 (3) Heat with conc. H_2SO_4 at 90° (4) PCl_5 (5) Acidified KMnO_4 (6) Acidified $\text{K}_2\text{Cr}_2\text{O}_7$. (Panjab T.D.C. Part I 1963)

CHAPTER XXXVI

DERIVATIVES OF MONOCARBOXYLIC ACIDS

A number of important compounds are obtained by the replacement of $-H$ or OH of the carboxyl group by other atoms or groups.

They are :

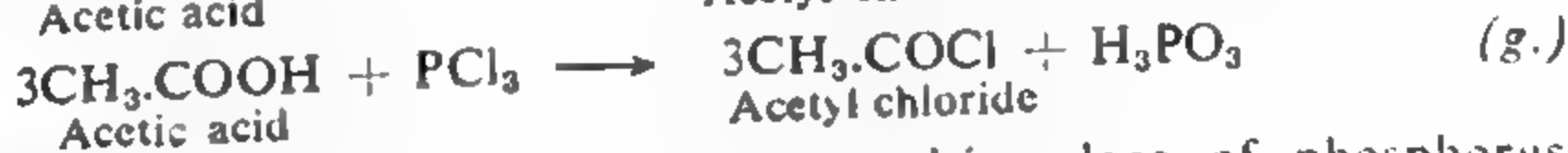
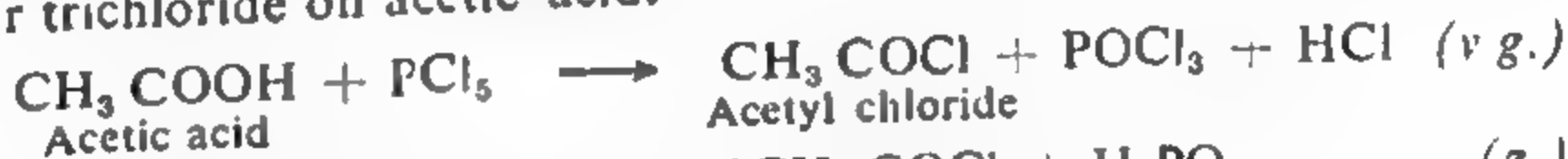
- (i) Acid chlorides, $R.COCl$
- (ii) Acid anhydrides, $R.CO.O.CO.R$
- (iii) Acid amides, $R.CONH_2$
- (iv) Esters, $RCOOR'$
- (v) Acid nitriles, $R.CN$

ACID CHLORIDES

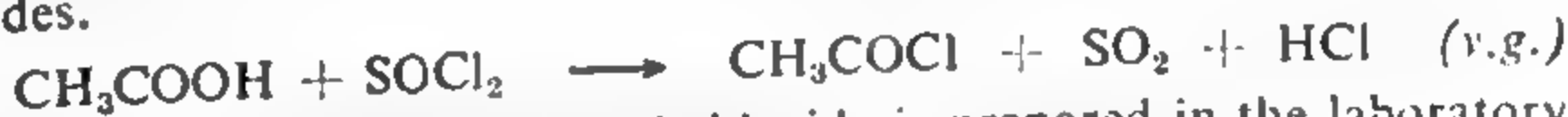
The most important acid chloride is acetyl chloride.

ACETYL CHLORIDE, $CH_3.COCl$

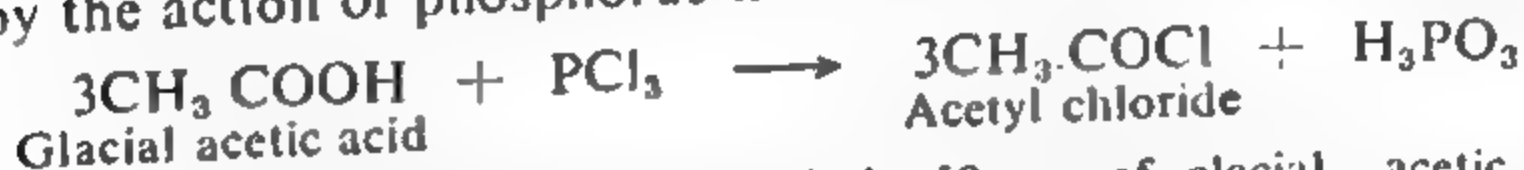
Acetyl chloride is prepared by the action of phosphorus pentachloride or trichloride on acetic acid.



Thionyl chloride, $SOCl_2$, may also be used in place of phosphorus chlorides.



Laboratory preparation. Acetyl chloride is prepared in the laboratory by the action of phosphorus trichloride on glacial acetic acid.



The apparatus used is shown in Fig.1. 50 gm. of glacial acetic acid is placed in a 250 ml. distillation flask fitted with a dropping funnel and a water condenser. The latter is connected to a receiver having a side tube which carries a guard tube containing fused calcium chloride in order to exclude the external moisture. 30 gm. of phosphorus trichloride is then transferred gradually to the flask through the dropping funnel. During the addition of phosphorus trichloride, the distillation flask

is kept cooled by immersing in cold water contained in the water bath. When the addition of phosphorus trichloride is complete, the temperature of the bath is raised to about 50° and maintained at this level till the evolution of hydrogen chloride slackens. The temperature is now raised to boiling and heating continued till no more acetyl chloride distils over. The receiver is kept in ice-cold water all the time. The acetyl chloride obtained above is further purified by redistillation, taking all precautions to exclude external moisture. The fraction distilling between $50-53^{\circ}$ is pure acetyl chloride.

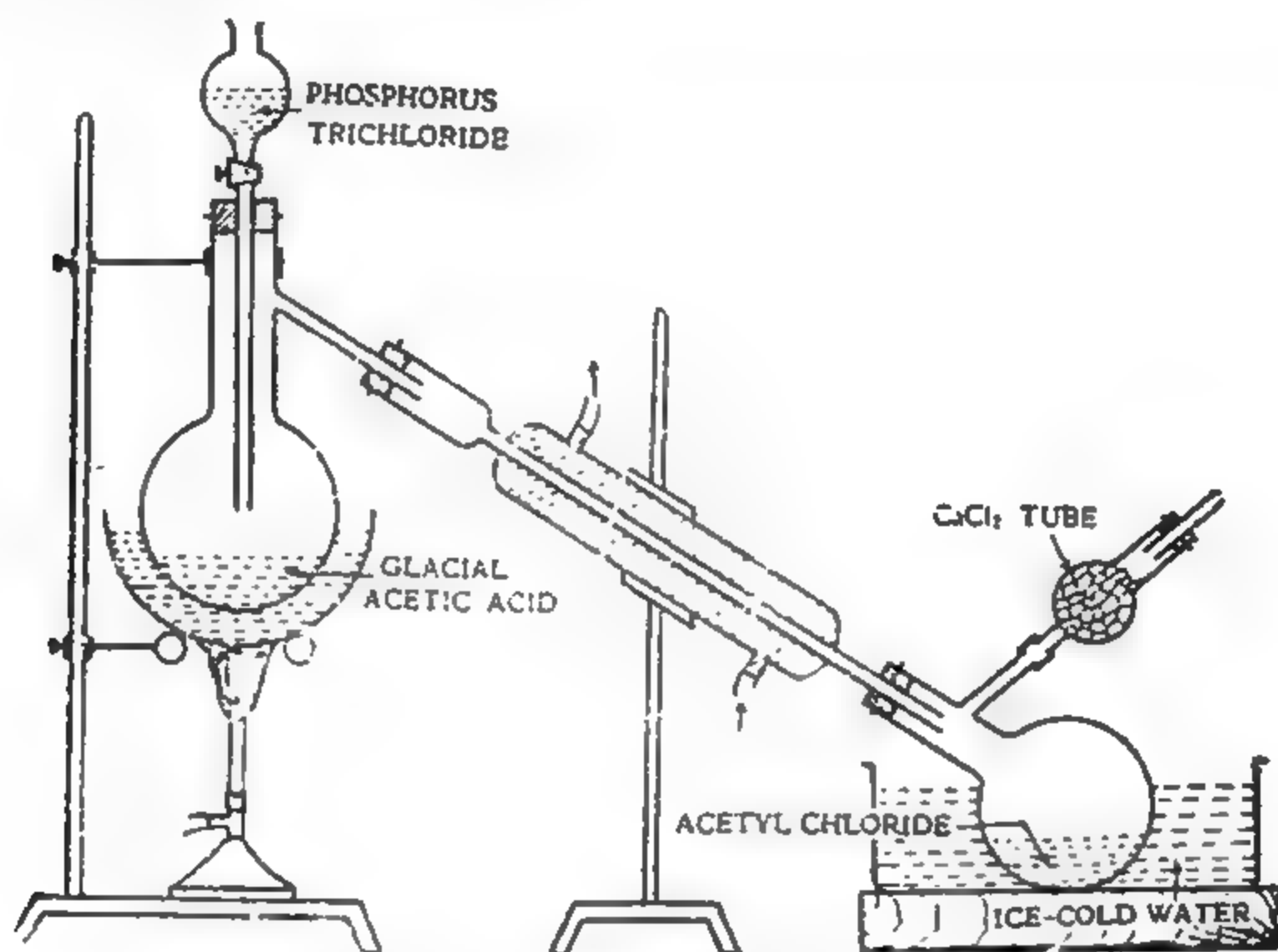


Fig. 1. Laboratory preparation of acetyl chloride.

Physical Properties. Acetyl chloride is a colourless, fuming liquid with a pungent odour. It boils at 52° . It is freely soluble in ether and chloroform.

Chemical Properties. The chlorine atom in acetyl chloride is extremely reactive. It can be easily replaced by other groups and atoms and hence a large number of compounds can be synthesised. The following are a few important examples.

1. Acetyl chloride is hydrolysed by water giving acetic acid.



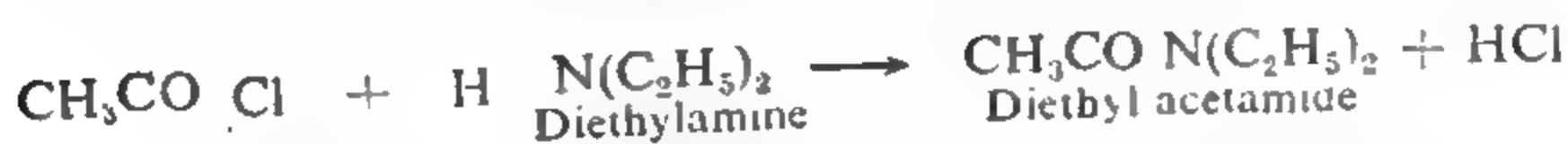
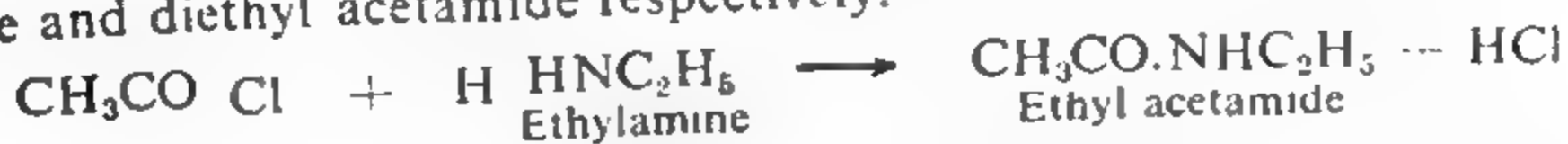
2. It reacts with alcohol forming ethyl acetate.



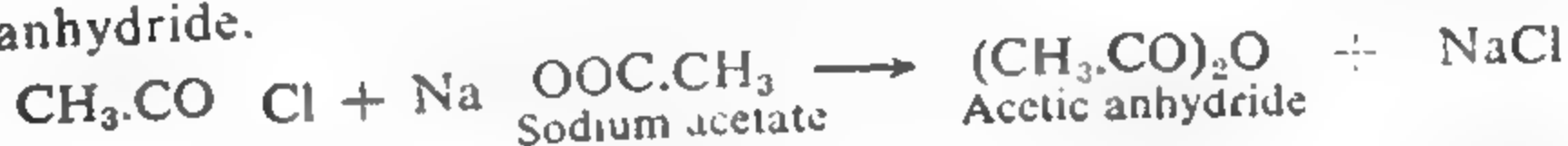
3. Acetyl chloride reacts with ammonia to form acetamide.



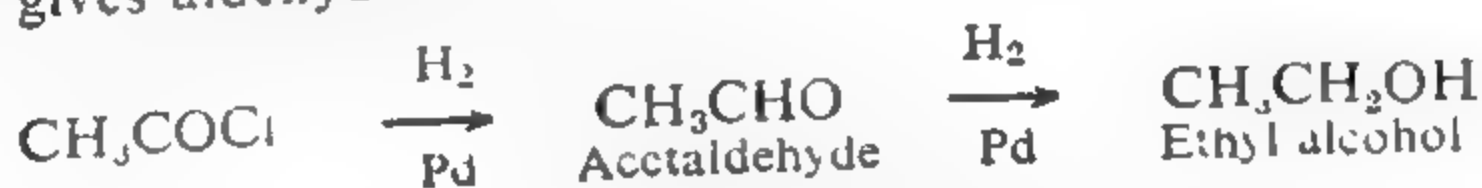
4. It reacts with ethylamine and diethylamine to form ethyl acetamide and diethyl acetamide respectively.



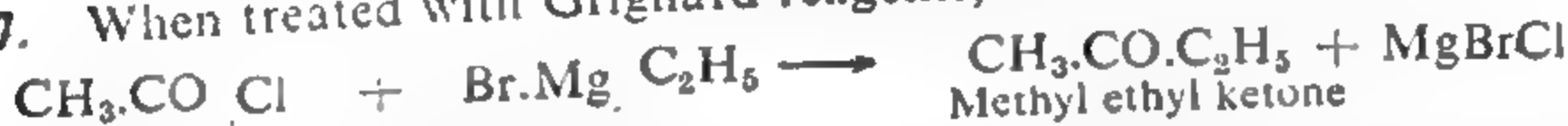
5. It readily attacks the sodium salts of fatty acids giving the anhydride.



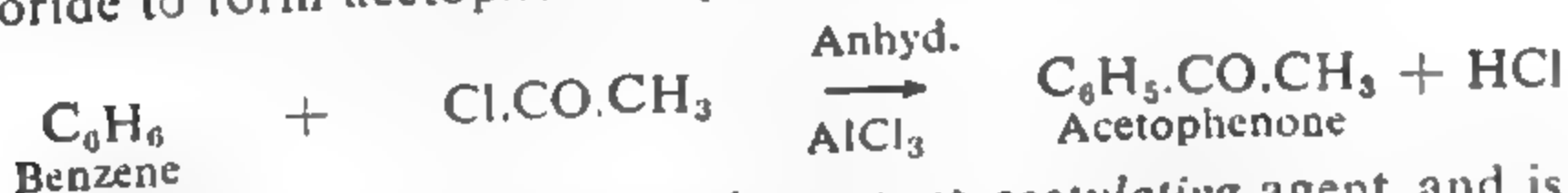
6. When reduced by hydrogen in the presence of palladium (catalyst) it gives aldehyde or alcohol.



7. When treated with Grignard reagents, it forms ketones.



8. It reacts with benzene in the presence of anhydrous aluminium chloride to form acetophenone (an aromatic ketone).

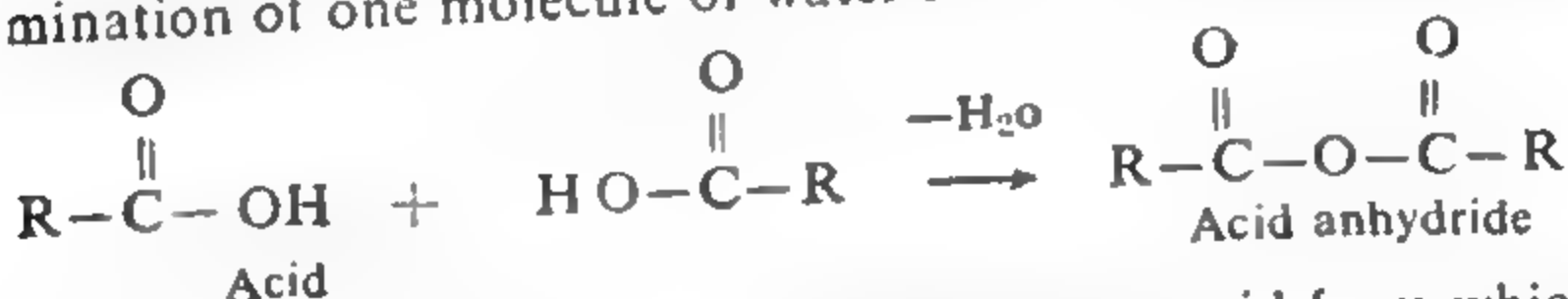


Uses. Acetyl chloride is an important *acetylating* agent and is used in large amounts in industry as well as in laboratory for introducing the acetyl group in compounds containing 'active hydrogen'.

It is also used for the detection and estimation of hydroxyl group in an organic compound.

ACID ANHYDRIDES

The acid anhydrides may be regarded as derived from acids by the elimination of one molecule of water from two molecules of the acid.



The anhydrides are named after the parent acid from which they are derived. For instance,

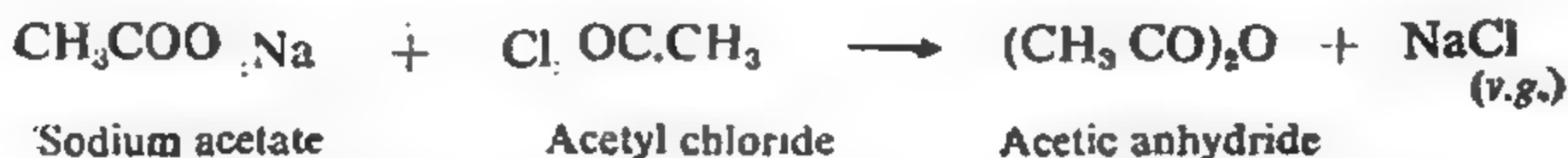
Acid	Anhydride
CH_3COOH , Acetic acid	$(\text{CH}_3\text{CO})_2\text{O}$, Acetic anhydride
$\text{C}_2\text{H}_5\text{COOH}$, Propionic acid	$(\text{C}_2\text{H}_5\text{CO})_2\text{O}$, Propionic anhydride

The most important acid anhydride is the acetic anhydride which is described below.

ACETIC ANHYDRIDE, $(\text{CH}_3\text{CO})_2\text{O}$

Preparation. Acetic anhydride may be prepared by the following methods :

(1) By distilling a mixture of anhydrous sodium acetate and acetyl chloride.



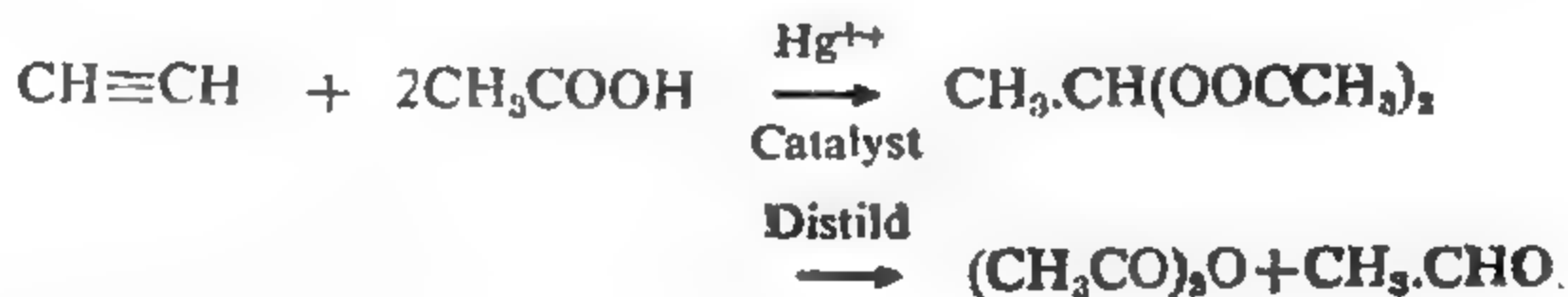
(2) By heating anhydrous sodium acetate with *controlled* amount of phosphorus trichloride, thionyl chloride or sulphuryl chloride. Half of the sodium acetate is converted into acetyl chloride which then reacts with the remaining half of the sodium acetate to form acetic anhydride.



(3) By passing chlorine into a mixture of sodium acetate and sulphur dichloride and then distilling.



(4) By passing acetylene into glacial acetic acid in the presence of a mercury salt (catalyst) and distilling the ethylidene diacetate formed to give acetic anhydride (industrial method).



Laboratory Preparation. Acetic anhydride is prepared in the laboratory by heating anhydrous sodium acetate with acetyl chloride.

The apparatus used is shown in Fig. 2. 50 gm. of anhydrous, powdered, sodium acetate is placed in a 250 ml. distillation flask fitted with a dropping funnel and a water condenser. The latter is connected to a receiver having a side tube which carries a guard tube containing fused calcium chloride in order to exclude the external moisture. 30 gm. of acetyl chloride is then transferred to the flask gradually through the dropping funnel keeping the flask well cooled. When the addition is complete, the distillation flask is heated on a direct flame. Heating is continued till no more of acetic anhydride distils over.

The distillate is then mixed with a little anhydrous sodium acetate and redistilled using an air condenser. Pure acetic anhydride is obtained between 135–140°.

Physical Properties. Acetic anhydride is a colourless, neutral liquid with an irritating smell, boiling at 139.5°. It is slightly soluble in water but freely soluble in ether and benzene.

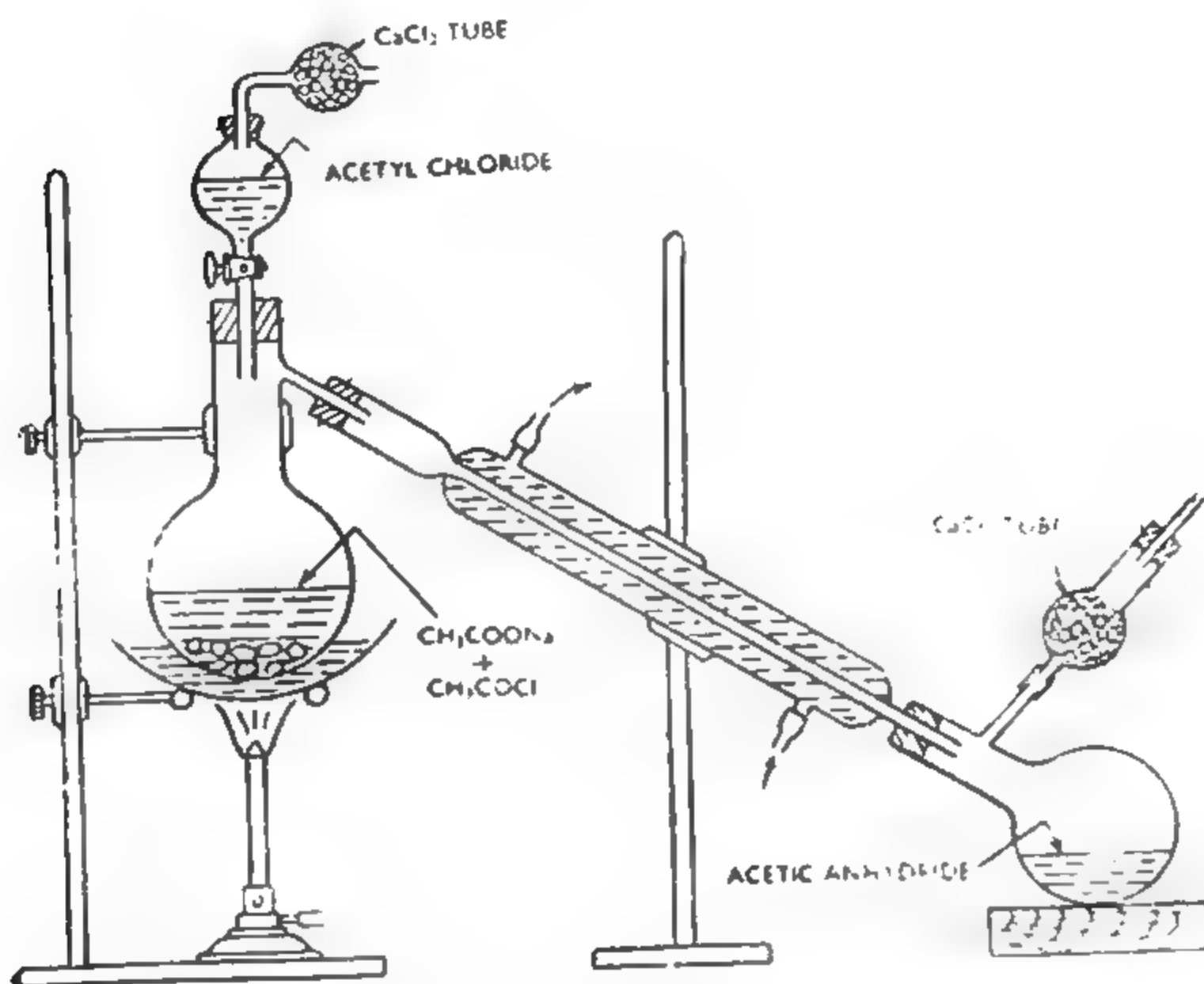


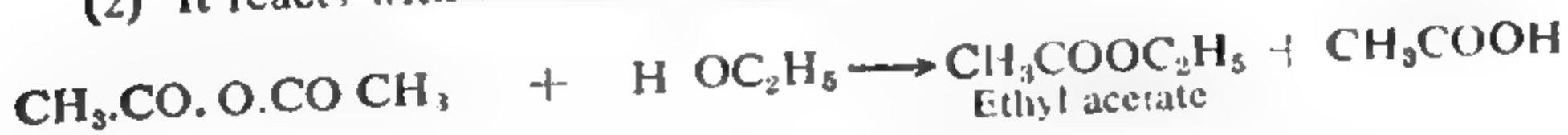
Fig. 2. Laboratory Preparation of Acetic anhydride

Chemical Properties. Acetic anhydride resembles acetyl chloride in its chemical behaviour and undergoes reactions similar to those of acetyl chloride but with less reactivity.

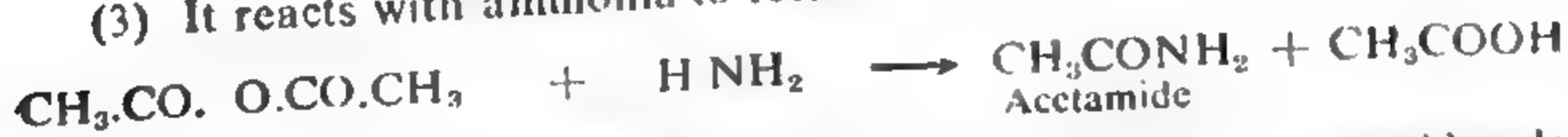
(1) Acetic anhydride is easily hydrolysed by water to give the parent acid.



(2) It reacts with alcohols to form esters.



(3) It reacts with ammonia to form amides.



(4) It reacts with hydrogen chloride and phosphorus pentachloride to form acetyl chloride.

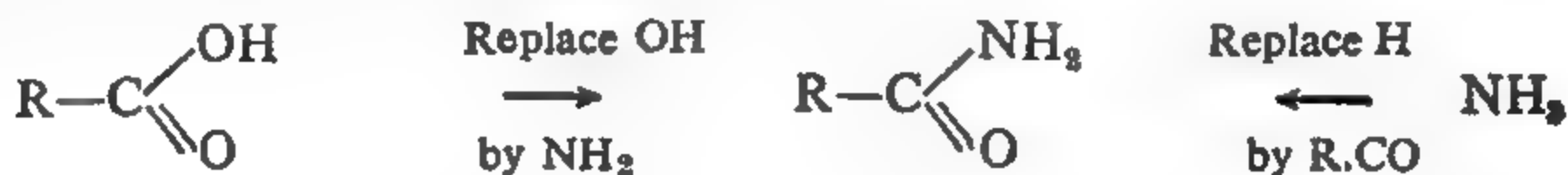




It is used as an acetylating agent.

ACID AMIDES

Acid amides may be regarded as derived from acids by the replacement of the hydroxyl group with the amino ($-\text{NH}_2$) group. Alternatively, amides may also be regarded as derived from ammonia by replacement of H-atom by the acyl group.



They are named after the parent acid from which they may be regarded as derived. For instance,

<i>Acid</i>		<i>Amide</i>
H.COOH, Formic acid		H.CONH ₂ , Formamide
CH ₃ .COOH, Acetic acid		CH ₃ .CONH ₂ , Acetamide
C ₂ H ₅ .COOH, Propionic acid		C ₂ H ₅ .CONH ₂ , Propionamide

The most important member of the series is acetamide.

ACETAMIDE, CH₃.CO.NH₂

The following methods are available for the preparation of acetamide :

(1) By heating ammonium acetate.



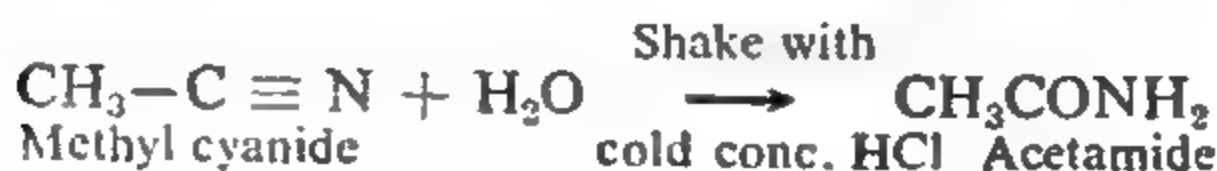
(2) By heating acetic acid with urea.



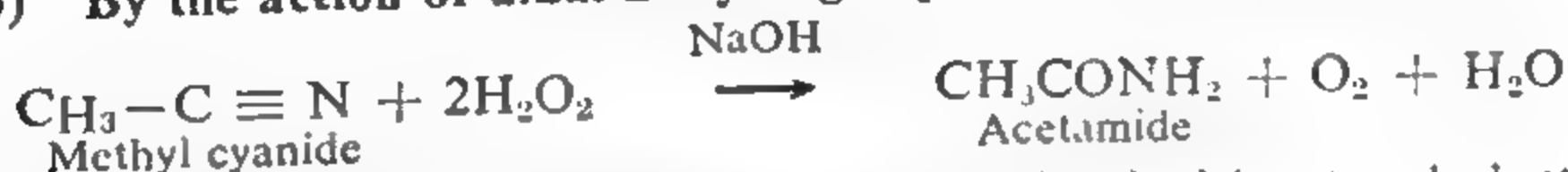
(3) By the action of concentrated ammonia solution on acetyl chloride, acetic anhydride or ethyl acetate.



(4) By the partial hydrolysis of methyl cyanide.



(5) By the action of alkaline hydrogen peroxide on methyl cyanide.



Laboratory Preparation. Acetamide is prepared in the laboratory by heating ammonium acetate in the presence of acetic acid.



Since ammonium acetate may decompose into ammonia and acetic acid on heating the reaction is best carried out by heating the ammonium acetate in the presence of acetic acid as the latter suppresses the dissociation of ammonium acetate.



Ammonium acetate crystals are boiled with an equal amount of glacial acetic acid under a reflux condenser for about 4 hours. The resulting product is then collected which is practically pure acetamide.

It may be further purified by recrystallising from acetone solution.

Physical Properties. Acetamide crystallises in the form of long colourless needles m.p. (82° and b.p. 222°). It is soluble in water and alcohol.

Chemical Properties. (1) **Hydrolysis.** Acetamide is hydrolysed, slowly by water, rapidly by acids and still more rapidly by alkalies, giving acetic acid.



(2) **Basic nature.** Acetamide behaves as a weak base and forms salts with strong acids. For example,



The salt, however, is unstable and is readily hydrolysed to give back the amide.

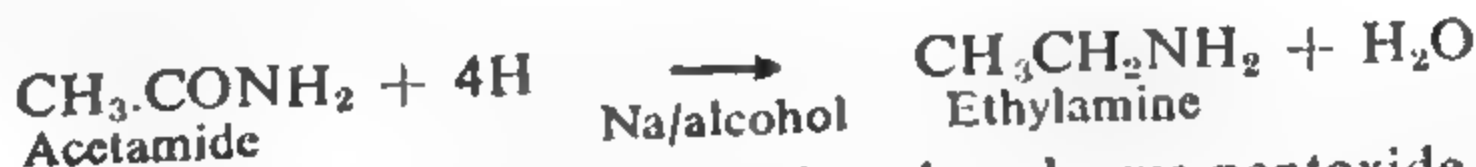
(3) **Acidic nature.** Acetamide also behaves as a weak acid. Thus, it forms salts with bases. For instance, it forms mercury salt with mercury oxide.



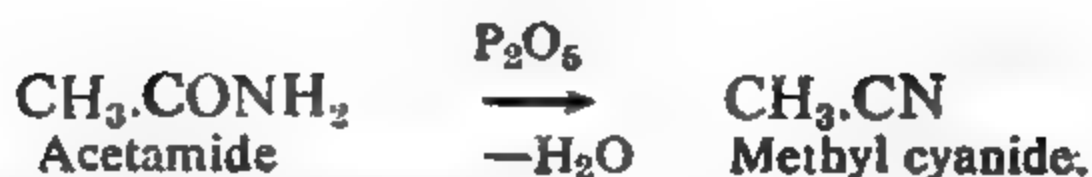
Similarly, when treated with sodium metal, acetamide forms sodium salt.



(4) **Reduction.** Acetamide is easily reduced to ethylamine (i) by sodium and alcohol (ii) catalytically (iii) by lithium—aluminium hydride.



(5) **Dehydration.** On heating with phosphorus pentoxide, acetamide loses a molecule of water giving methyl cyanide.



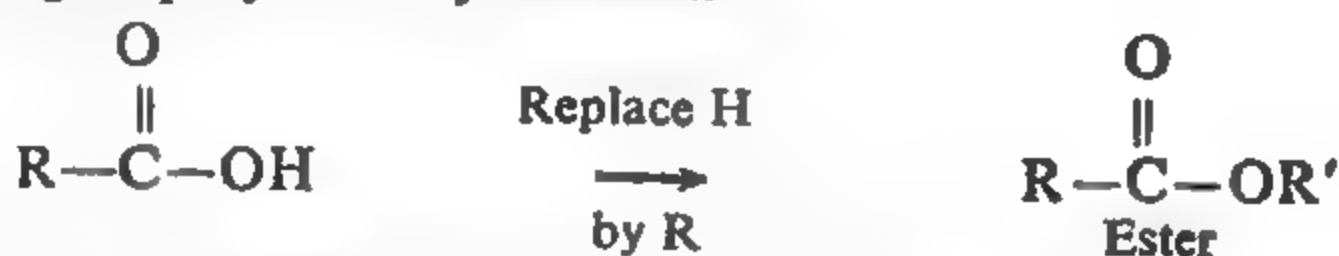
(6) **Hofmann's bromamide reaction.** Acetamide, when treated with bromine and sodium hydroxide, yields methyl amine having one carbon atom less than the amide.



For mechanism of Hofmann's bromamide reaction refer to p. 490.

ESTERS

Esters are derived from acids by the replacement of the H-atom of the carboxyl group by an alkyl radical.



They are named as the alkyl salts of the acids. For example,

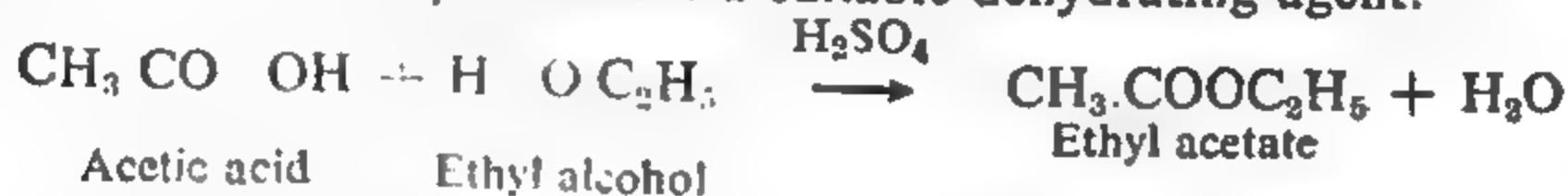


The best representative of esters is ethyl acetate.

ETHYL ACETATE, $\text{CH}_3\text{COOC}_2\text{H}_5$

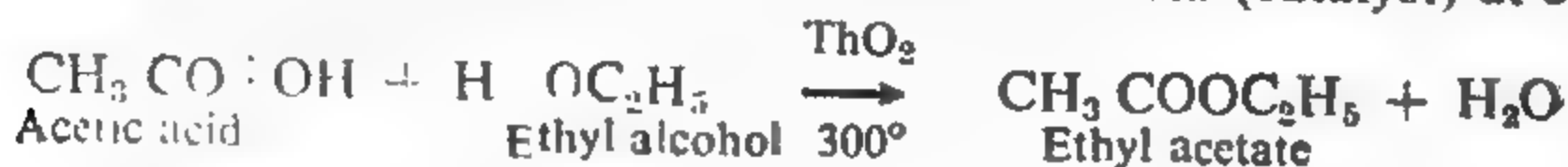
Preparation. The following methods are available for the preparation of ethyl acetate.

(1) **Direct esterification.** The most common method for the preparation of ethyl acetate is the direct combination of acetic acid and ethyl alcohol in the presence of a suitable dehydrating agent.



Sulphuric acid is added to take up water formed during the reaction. If this is not done, the reaction becomes reversible.

Esterification may also be carried out by passing a mixture of the vapours of ethyl alcohol and acetic acid over thoria (catalyst) at 300° .



(2) **Esterification of ethyl alcohol by acetyl chloride or acetic anhydride.** Acetyl chloride or acetic anhydride readily attacks ethyl alcohol giving ethyl acetate.

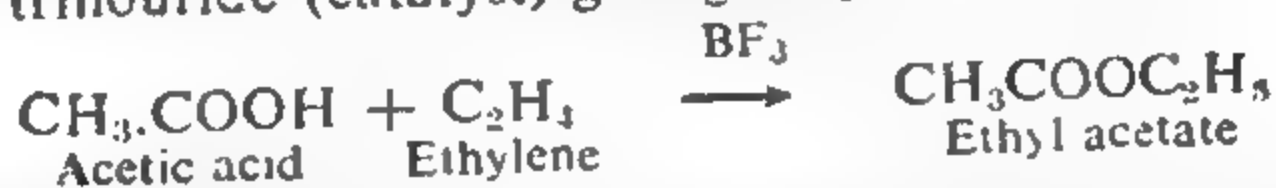




(3) **From silver acetate.** Ethyl acetate can also be obtained by treating silver acetate with ethyl halide.



(4) **From ethylene.** Acetic acid reacts with ethylene in the presence of boron trifluoride (catalyst) giving ethyl acetate.

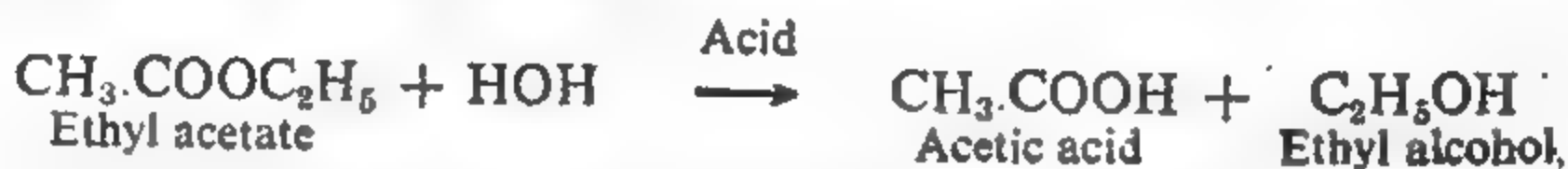


flask gradually at such a rate that the temperature is maintained at 140° . The distillation is continued for about 10 minutes after the complete addition of the alcohol-acid mixture.

The distillate is then transferred to a separating funnel and shaken with a solution of sodium carbonate to neutralise the acid. The lower aqueous layer is run out. The reaction mixture is then treated with a saturated solution of calcium chloride to remove the alcohol and the lower aqueous layer again run out. The ethyl acetate is then washed with water and dehydrated over fused calcium chloride and then distilled. The fraction distilling between $74-79^{\circ}$ is collected. This gives almost pure ethyl acetate.

Physical Properties. Ethyl acetate is a colourless liquid having a characteristic fruity smell. It boils at 78° . It is sparingly soluble in water but is readily soluble in organic solvents. Itself, it is a good solvent.

Chemical Properties. (1) **Hydrolysis.** Ethyl acetate is easily hydrolysed by acids as well as alkalies



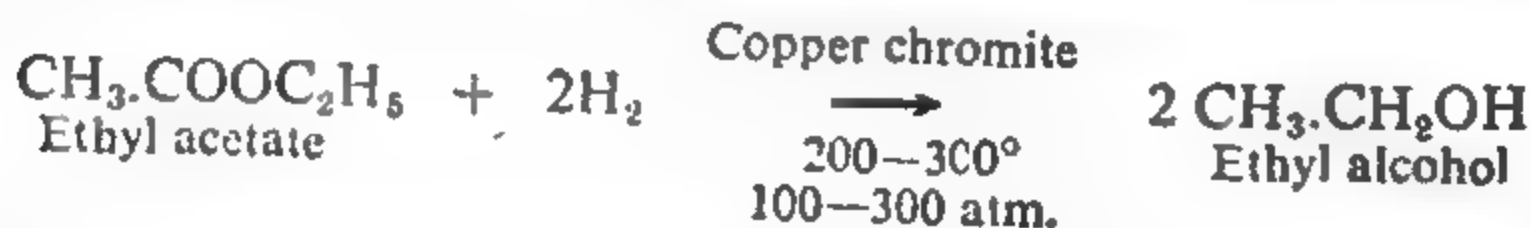
The hydrolysis with alkalies is far more rapid than the hydrolysis with acids.

Since the alkali salts of higher fatty acids are soaps, the alkaline hydrolysis is also known as **saponification**.

(2) **Reduction.** Ethyl acetate is easily reduced to ethyl alcohol by nascent hydrogen.



The reduction can also be carried out by molecular hydrogen at 100–300 atmospheres in the presence of copper chromite (catalyst) at $200-300^{\circ}$.



(3) **Reaction with ammonia.** Ethyl acetate reacts with ammonia giving acetamide.



(4) **Reaction with phosphorus pentachloride.** Ethyl acetate is readily decomposed by phosphorus pentachloride giving acetyl chloride and ethyl chloride.



Uses. Ethyl acetate is used as a solvent in the manufacture of smokeless powders. On account of its refreshing odour, it is largely employed in the preparation of artificial fruit essences.

SUMMARIES OF TYPICAL MEMBERS

PREPARATION AND PROPERTIES OF ACETYL CHLORIDE

Preparation.

Acetic acid
 CH_3COOH

PCl_5 or PCl_3
or SOCl_2

Acetyl Chloride
 CH_3COCl

Properties.

Hydrolysis

Acetic acid
 CH_3COOH

$\text{C}_2\text{H}_5\text{OH}$

Ethyl Acetate
 $\text{CH}_3\text{COOC}_2\text{H}_5$

NH_3

Acetamide
 CH_3CONH_2

$\text{C}_2\text{H}_5\text{NH}_2$

Ethyl acetamide
 $\text{CH}_3\text{CO.NH.C}_2\text{H}_5$

Acetyl chloride
 CH_3COCl

$(\text{C}_2\text{H}_5)_2\text{NH}$

Diethyl acetamide
 $\text{CH}_3\text{CO.N}(\text{C}_2\text{H}_5)_2$

CH_3COONa distil

Acetic anhydride
 $(\text{CH}_3\text{CO})_2\text{O}$

Reduction (H_2/Pd)

Acetaldehyde
 CH_3CHO

$\downarrow \text{H}_2$

Ethyl Alcohol
 $\text{C}_2\text{H}_5\text{OH}$

$\text{C}_2\text{H}_5\text{MgBr}$

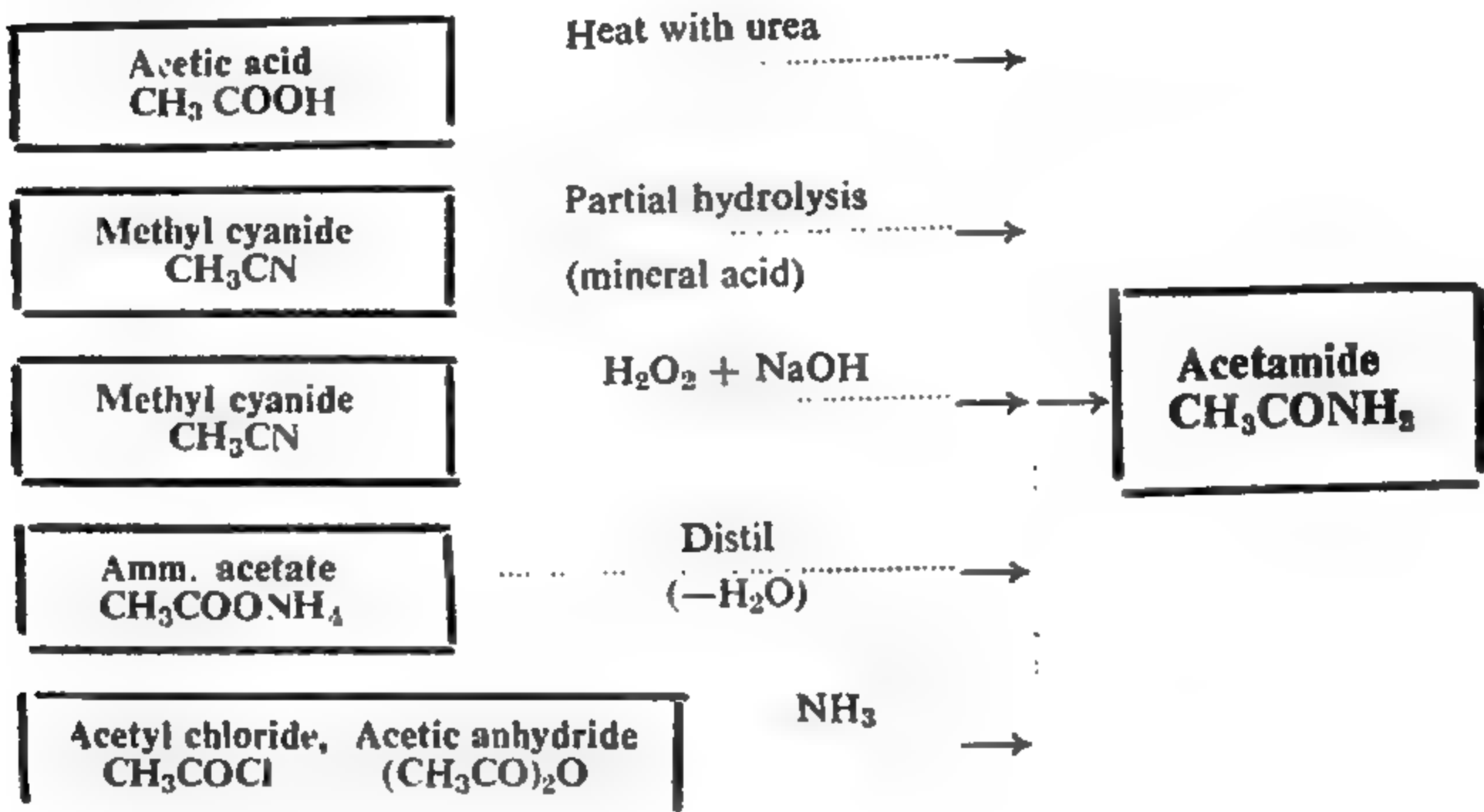
Methyl ethyl ketone
 $\text{CH}_3\text{CO.C}_2\text{H}_5$

$\text{C}_6\text{H}_6/(\text{AlCl}_3 \text{ anhy.})$

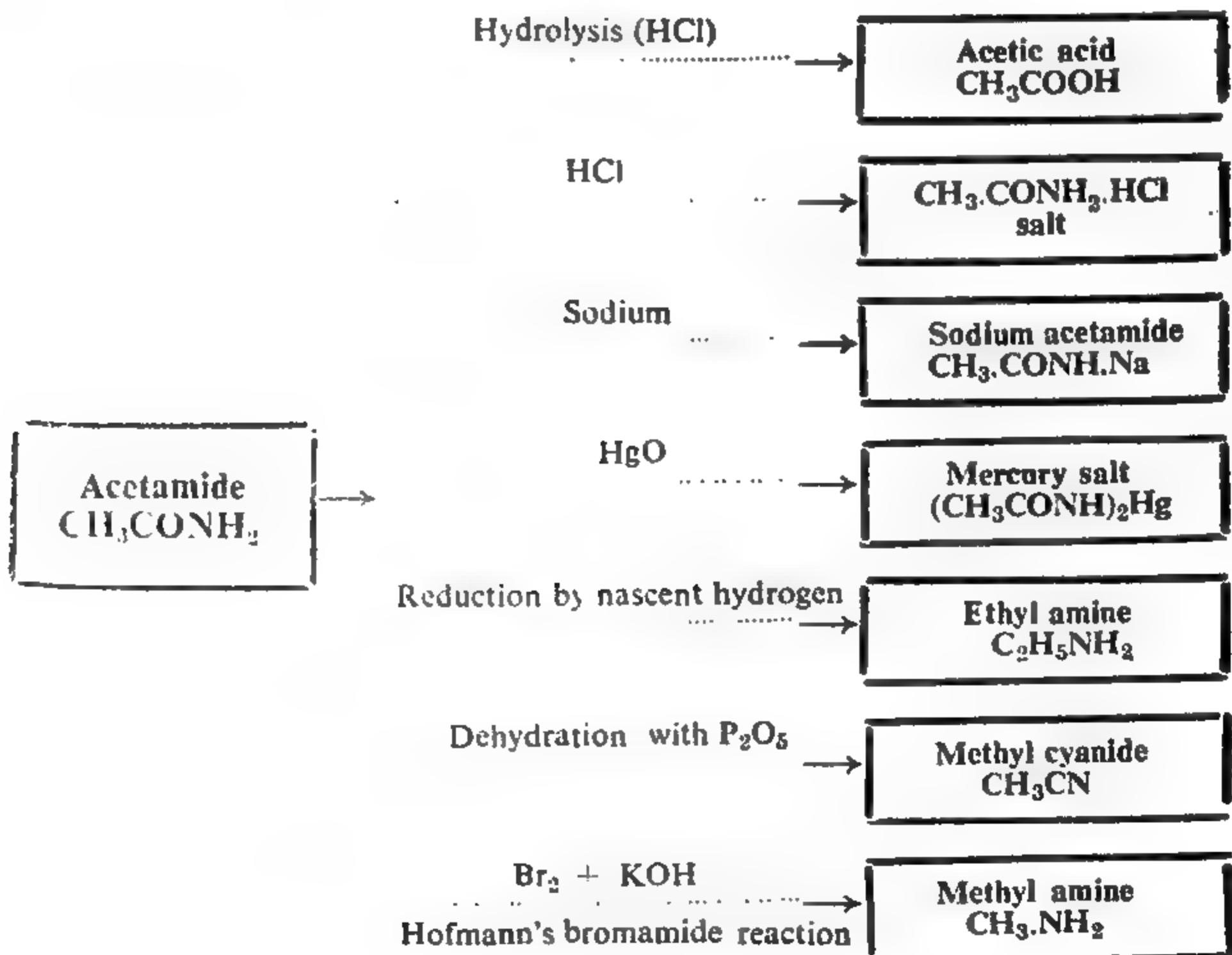
Acetophenone
 $\text{C}_6\text{H}_5\text{CO.CH}_3$

PREPARATION AND PROPERTIES OF ACETAMIDE

Preparation.

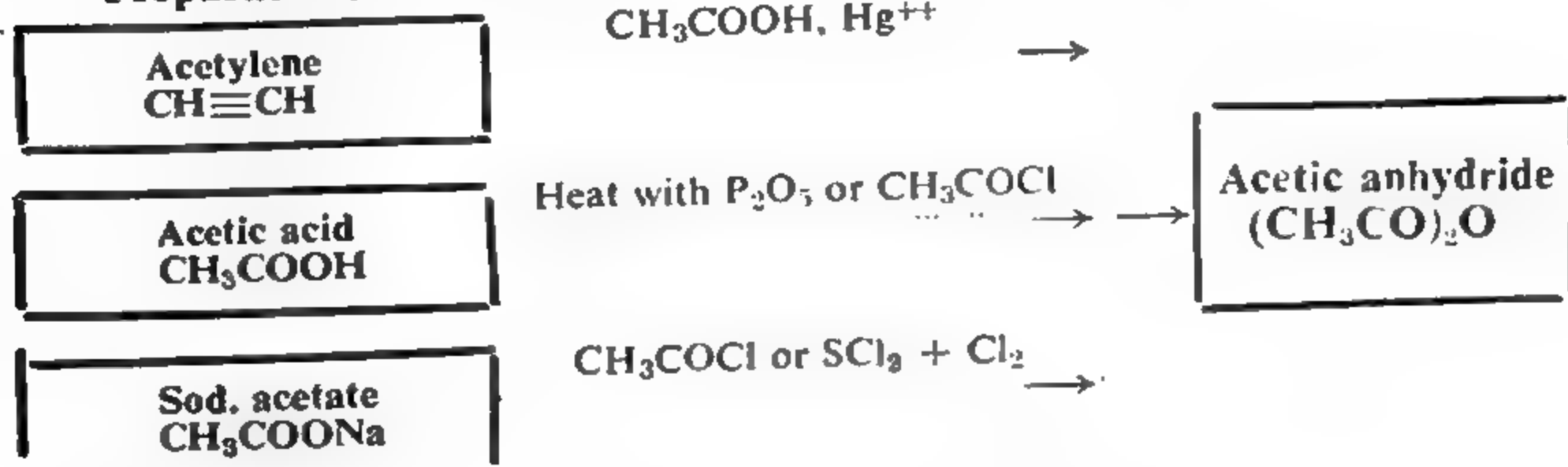


Properties.

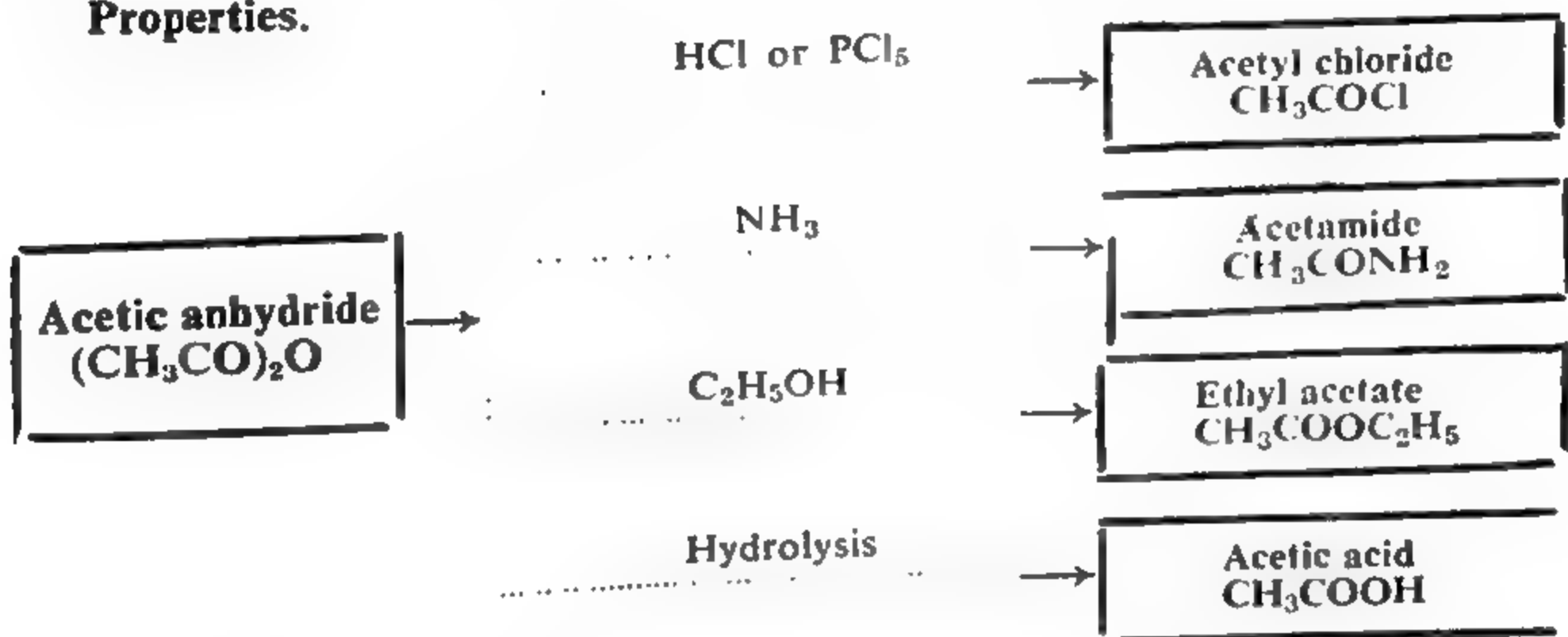


PREPARATION AND PROPERTIES OF ACETIC ANHYDRIDE

Preparation.

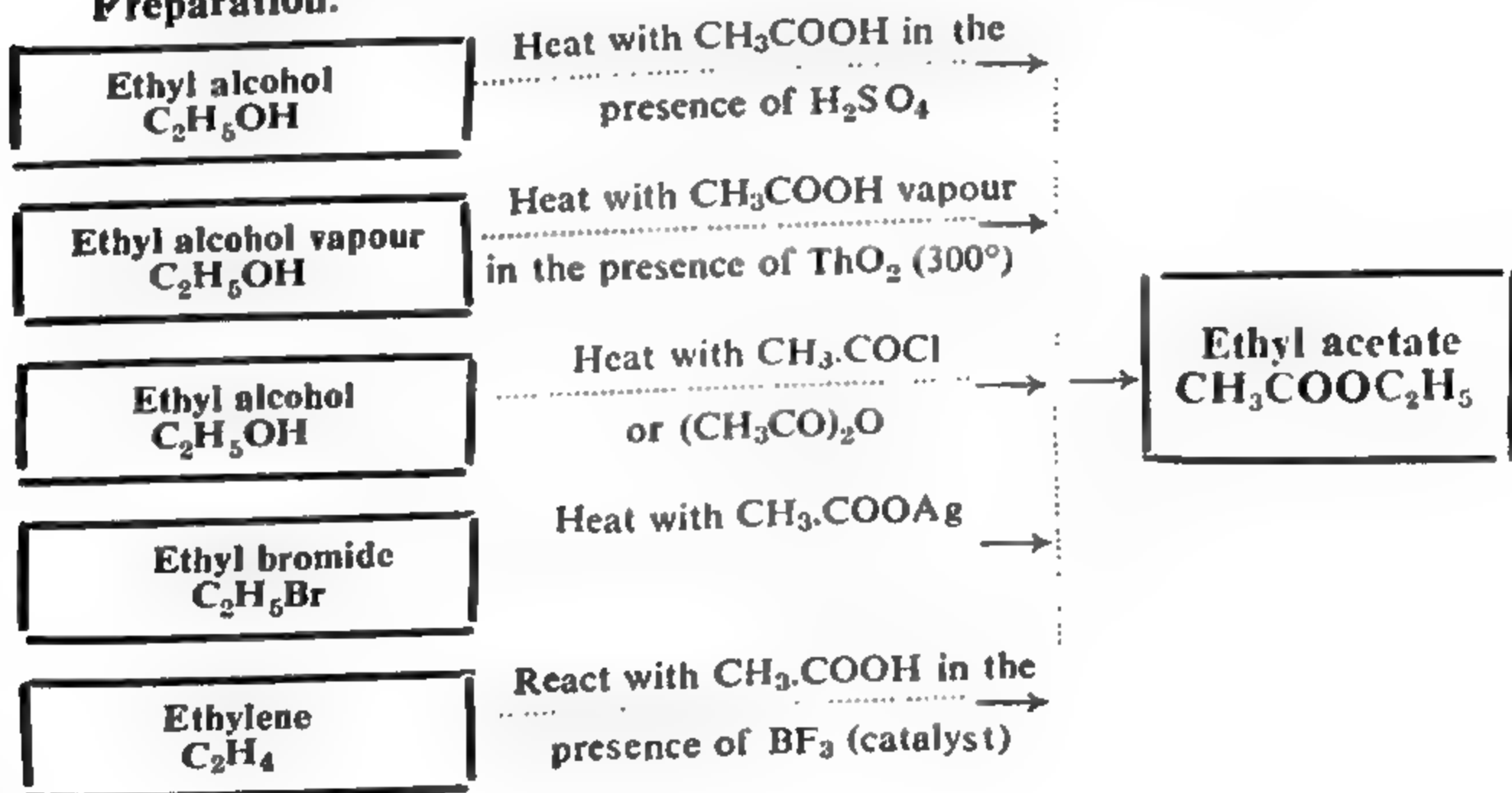


Properties.

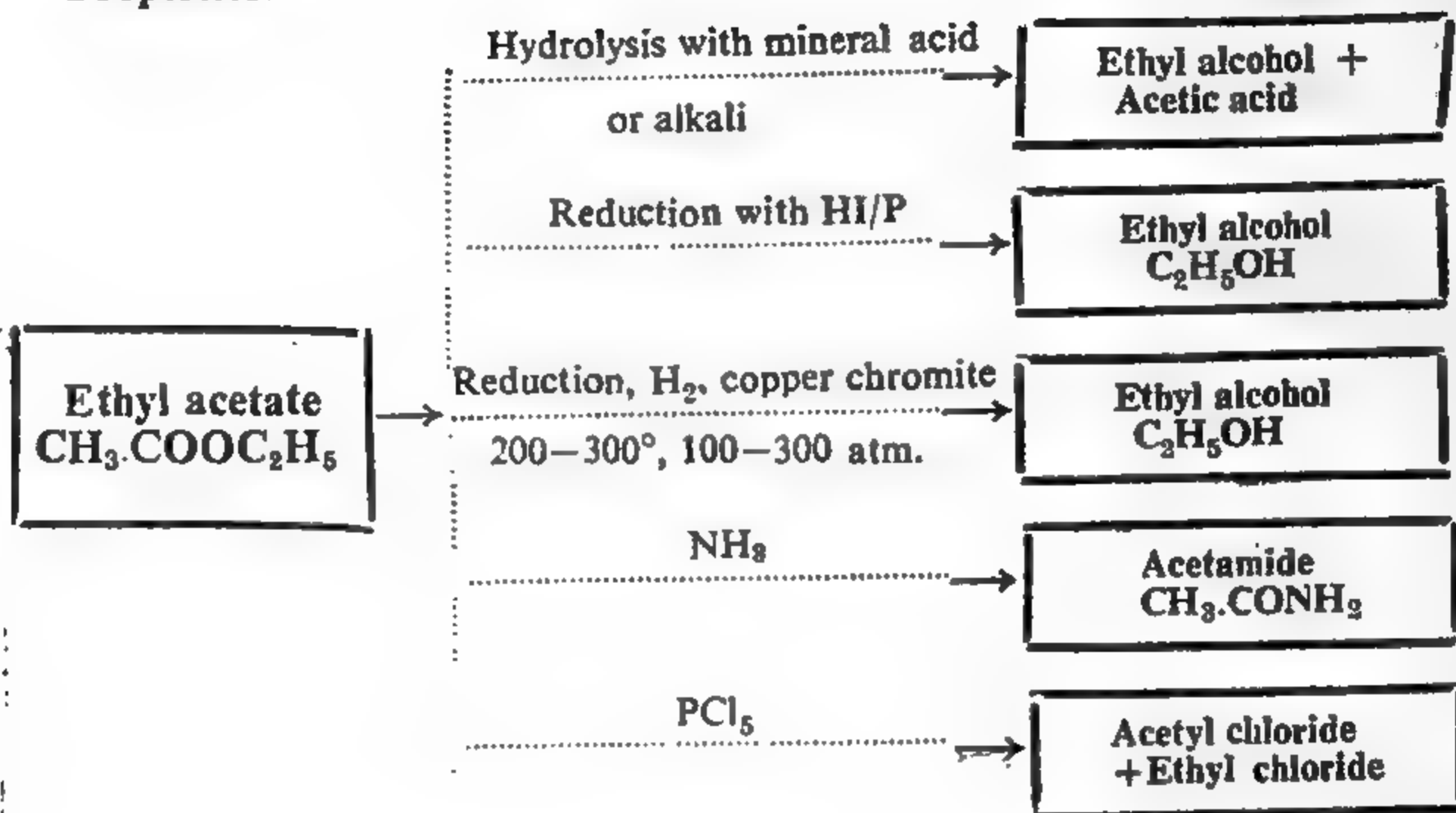


PREPARATION AND PROPERTIES OF ETHYL ACETATE

Preparation.



Properties.



QUESTIONS

1. What are acid chlorides, acid amides, acid anhydrides and esters? Give the type formula and the name of the important representative member of each class.

2. How is acetyl chloride prepared in the laboratory? Give its important properties and uses.

3. Give practical details for the preparation of acetyl chloride. How can it be converted into:

(i) Acetic acid (ii) Ethyl acetate (iii) Acetamide (iv) Acetic anhydride
(v) Acetaldehyde (vi) Ethyl alcohol (vii) Acetone and (viii) Acetophenone?

4. How is acetic anhydride prepared in the laboratory? How can it be converted into acetic acid, ethyl acetate, acetamide, acetyl chloride, and methyl acetamide?

5. Give the various methods for the preparation of acetamide. Describe its important properties and uses.

6. Describe the laboratory preparation of acetamide. How can it be converted into:

(i) Acetic acid (ii) Ethyl amine (iii) Methylamine (iv) Methyl cyanide?

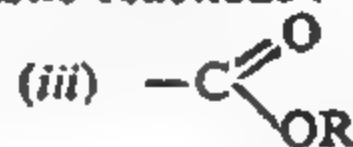
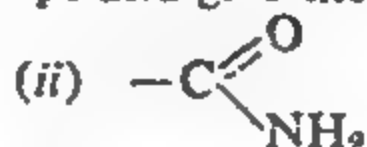
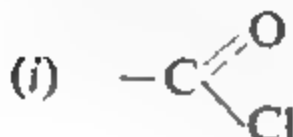
Show that an amide behaves both as a weak acid and a weak base.

7. What are esters? Describe the methods for the preparation of ethyl acetate and its important properties.

8. Give the practical details for the preparation of ethyl acetate. How can it be converted into acetic acid, ethyl alcohol, acetamide, and acetyl chloride?

Describe the important uses of ethyl acetate.

9. Name the following groups and give their characteristic reactions:



10. What is an acid chloride? Name some acid chloride and give an account of its preparation and properties. (Panjab Inter 1950)

11. Distinguish chemically between acetyl chloride and acetic anhydride. (Panjab Inter 1951)

CHAPTER XXXVII

ORGANIC DERIVATIVES OF INORGANIC ACIDS

The important derivatives of carboxylic acids have been described in the previous chapter. In the following pages, the important derivatives of inorganic acids such as nitric, nitrous, sulphuric, hydrocyanic and carbonic acids have been discussed.

DERIVATIVES OF NITRIC ACID

Alkyl Nitrates. $R.O.NO_2$. These are regarded as obtained by the replacement of H-atom of nitric acid by the alkyl radical.



For example,



The alkyl nitrates may, therefore, be regarded as the esters of nitric acid. The typical member, ethyl nitrate, is described below :

ETHYL NITRATE, $C_2H_5O.NO_2$

Preparation. (1) Ethyl nitrate is prepared by heating ethyl iodide with silver nitrate.



Ethyl iodide

(2) It may also be prepared by the action of concentrated nitric acid on ethyl alcohol in the presence of urea.



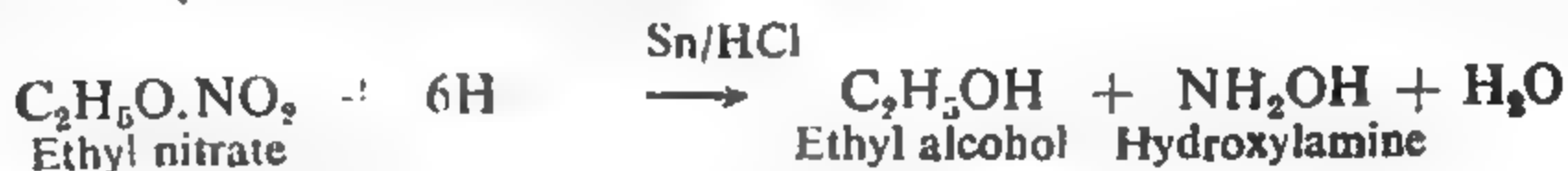
In this reaction a part of the alcohol is oxidised and the nitric acid is reduced to nitrous acid. The urea present destroys this nitrous acid otherwise the reaction becomes very violent.

Physical Properties. Ethyl nitrate is a colourless liquid (b.p. 88°), having a pleasant smell. It is insoluble in water.

Chemical Properties. (1) **Hydrolysis.** On boiling with an alkali or water, ethyl nitrate is hydrolysed to give ethyl alcohol.

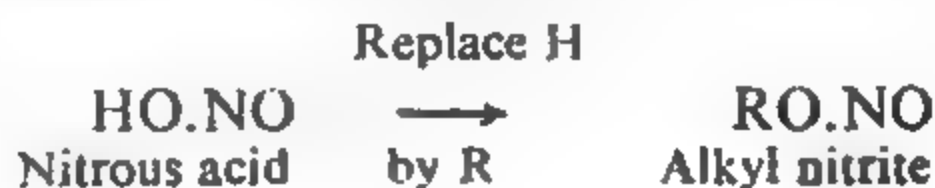


(2) **Reduction.** With tin and hydrochloric acid, ethyl nitrate is reduced to ethyl alcohol and hydroxylamine.



DERIVATIVES OF NITROUS ACID

Alkyl Nitrites, RO.NO. These are regarded as obtained by the replacement of H-atom of nitrous acid by the alkyl radicals.



For example,



Alkyl nitrites may, therefore, be regarded as **esters of nitrous acid**. The most important member is ethyl nitrite.

ETHYL NITRITE, $\text{C}_2\text{H}_5\text{O.NO}$

Preparation, (1) Ethyl nitrite is obtained by adding concentrated hydrochloric acid or sulphuric acid to a mixture of ethyl alcohol and aqueous sodium nitrite.



(2) It may also be obtained by the action of nitrogen trioxide on ethyl alcohol.



Physical Properties. Ethyl nitrite is a pleasant smelling liquid, boiling at 17° . At ordinary temperatures, therefore, it is in the gaseous state. It is soluble in water.

Chemical Properties. (1) **Hydrolysis.** On treatment with aqueous alkali, it is readily hydrolysed to give ethyl alcohol.



(2) **Reduction.** With tin and hydrochloric acid, it is reduced to ethyl alcohol.

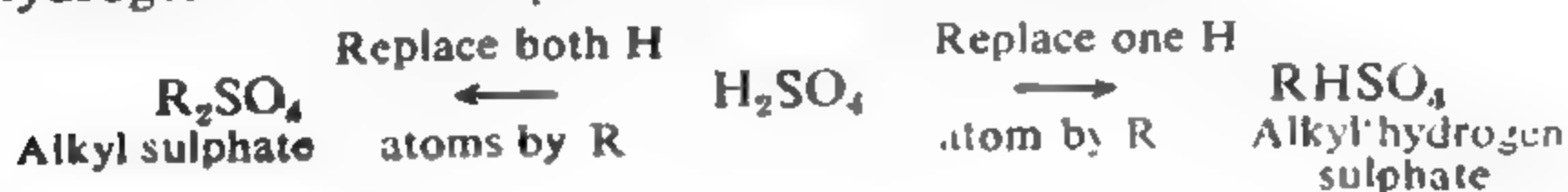


Uses. (1) Ethyl nitrite is used as medicine in the treatment of asthma and heart diseases.

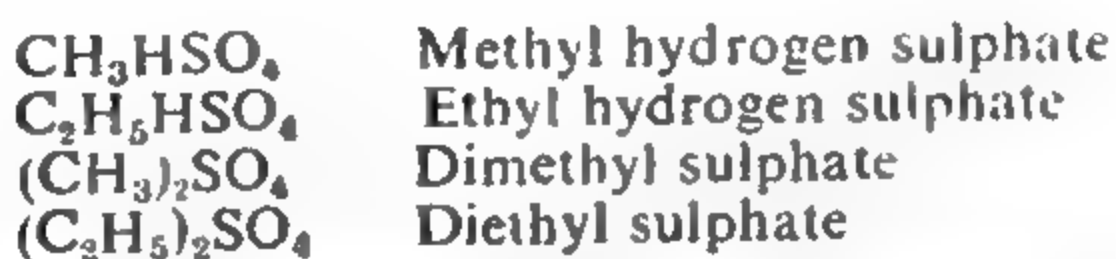
(2) Since it readily decomposes to give nitrous acid, it is used as a source of nitrous acid in organic reactions.

DERIVATIVES OF SULPHURIC ACID

Alkyl Hydrogen Sulphates, RHSO_4 and Alkyl Sulphates, R_2SO_4 . These are regarded as obtained by the replacement of one or both the hydrogen atoms of sulphuric acid by alkyl radicals.



For instance,



These may, therefore, be regarded as **esters of sulphuric acid**.

The important members are ethyl hydrogen sulphate and dimethyl sulphate.

ETHYL HYDROGEN SULPHATE, Ethyl Sulphuric acid, $\text{C}_2\text{H}_5\text{HSO}_4$

Preparation. (1) Ethyl hydrogen sulphate can be easily prepared by heating ethyl alcohol with concentrated sulphuric acid at 100° .



(2) It may also be prepared by absorbing ethylene in sulphuric acid.

Physical Properties. Ethyl hydrogen sulphate is an oily liquid possessing no smell. It is miscible with water in all proportions.

Chemical Properties. The important reactions of ethyl hydrogen sulphate are :

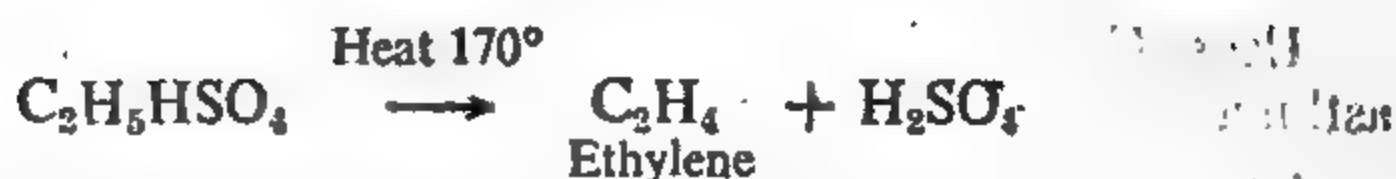
(1) **Hydrolysis.** On boiling with water, it is hydrolysed to give alcohol.



(2) **Decomposition.** (i) When heated alone, it decomposes to give diethyl sulphate and sulphuric acid.



(ii) On heating with excess of sulphuric acid at 170° , it decomposes to give ethylene.



(iii) On heating with alcohol at 140° , it gives ether.



(3) **Acidic nature.** Ethyl hydrogen sulphate decomposes carbonates and bicarbonates giving carbon dioxide, showing that it is acidic in nature.

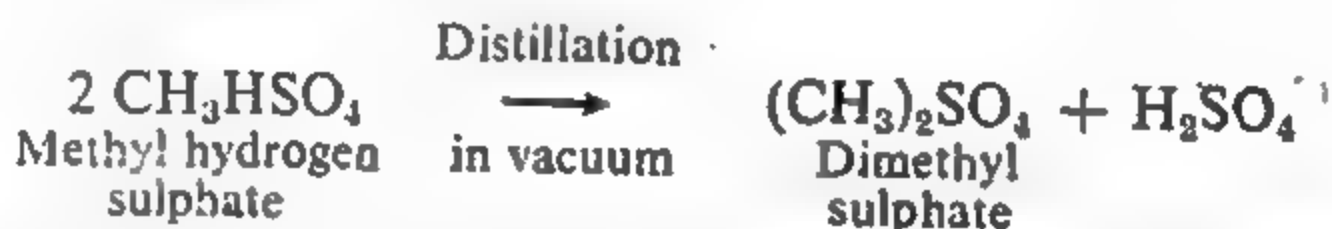


The sodium and potassium salts of ethyl hydrogen sulphate are extremely reactive and can be used for the preparation of several ethyl derivatives, as illustrated below :



METHYL SULPHATE $(\text{CH}_3)_2\text{SO}_4$

Preparation. (1) Methyl sulphate is obtained by distilling methyl hydrogen sulphate under reduced pressure.



(2) Industrially, it is prepared by passing sulphur trioxide into methyl alcohol at low temperatures.



(3) It may also be obtained by heating methyl iodide with silver sulphate.



Physical Properties. Methyl sulphate (b.p. 188°) is a heavy, colourless, odourless liquid which is immiscible with water. It is extremely poisonous.

Chemical Properties. (1) It is readily hydrolysed by alkalies forming methyl alcohol.



(2) It readily attacks the hydroxy compounds (alcohols and phenols) as well as the amino compounds, giving the corresponding methyl derivatives. For example,



Because of the above reactions, dimethyl sulphate is commonly employed as a **methylating agent**, that is, for introducing methyl group in alcohols, phenols, amines, etc.

Ethyl Sulphate, $(\text{C}_2\text{H}_5)_2\text{SO}_4$

It can be prepared by the same methods as employed for the preparation of methyl sulphate. It is prepared on a commercial scale by passing ethylene in cold concentrated sulphuric acid.



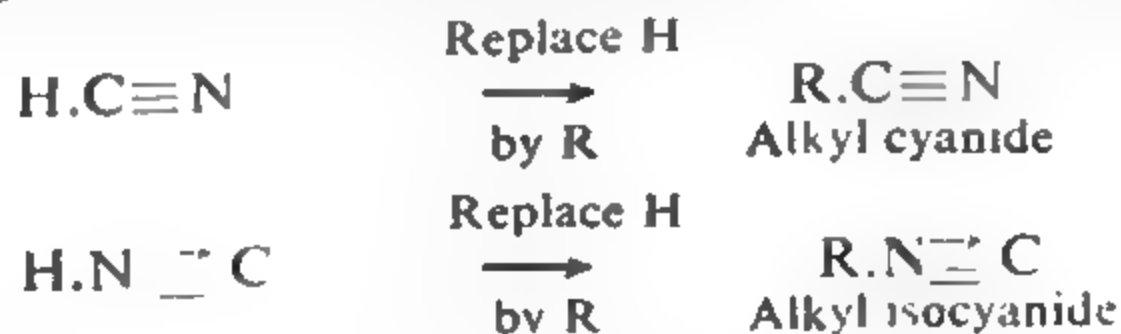
Ethyl sulphate is a colourless, odourless heavy liquid boiling at 208° and is also extremely poisonous. It gives the same reactions as given by methyl sulphate and is used as an **ethylating agent**.

DERIVATIVES OF HYDROCYANIC ACID

Alkyl Cyanides and Isocyanides. Hydrocyanic acid (HCN) is known to exist in two tautomeric forms, *viz.*,



Hence, two types of alkyl derivatives can be obtained. Those derived by the replacement of H-atom of the hydrogen cyanide by the alkyl radicals are known as **alkyl cyanides** and those obtained by the replacement of H-atom of hydrogen isocyanide are known as **alkyl isocyanides**.



For instance,

CH_3CN , Methyl cyanide ;

$\text{C}_2\text{H}_5\text{CN}$, Ethyl cyanide ;

CH_3NC , Methyl isocyanide

$\text{C}_2\text{H}_5\text{NC}$, Ethyl isocyanide

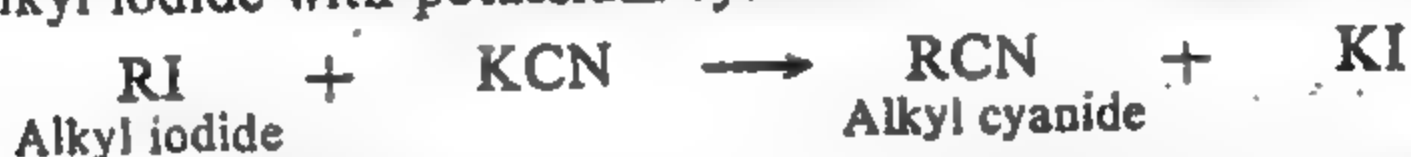
These may also be regarded as derived from carboxylic acids by the replacement of the carboxyl group ($-\text{COOH}$) by the cyanide or the isocyanide group. Hence they are also named as **acid nitriles** or **acid isonitriles**, as the case may be.



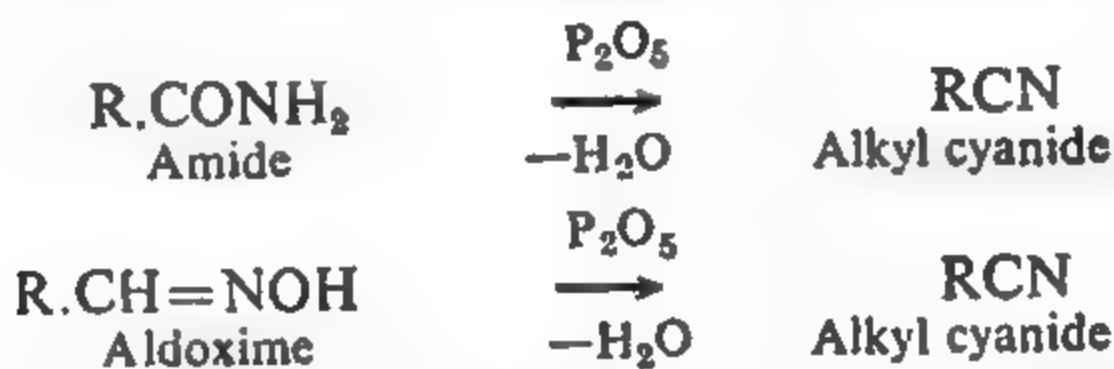
For instance, CH_3CN is known as **aceto-nitrile** and CH_3NC is named as **aceto-isonitrile**.

ALKYL CYANIDES OR ACID NITRILES, $\text{R}-\text{C}\equiv\text{N}$

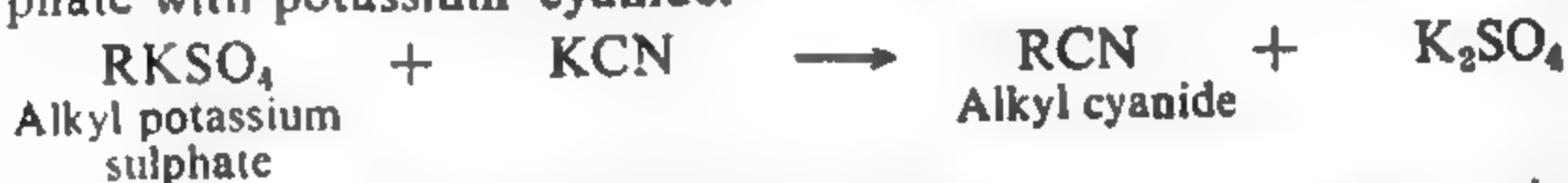
Preparation. (1) Alkyl cyanides are conveniently prepared by heating an alkyl iodide with potassium cyanide in dilute alcohol solution.



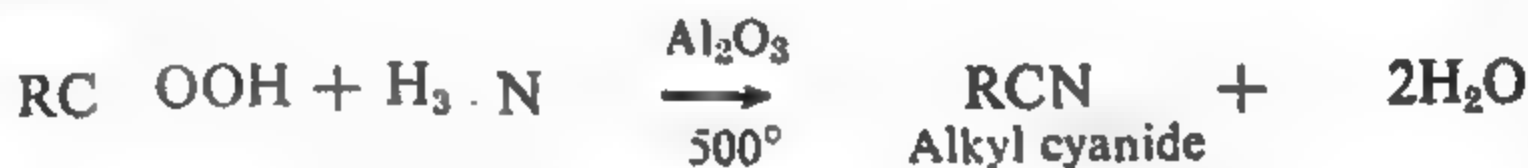
(2) Alkyl cyanides can also be prepared by the dehydration of amides and aldoximes with phosphorus pentoxide.



(3) Many cyanides, particularly the lower members, can be conveniently and readily obtained by warming the potassium or sodium alkyl sulphate with potassium cyanide.



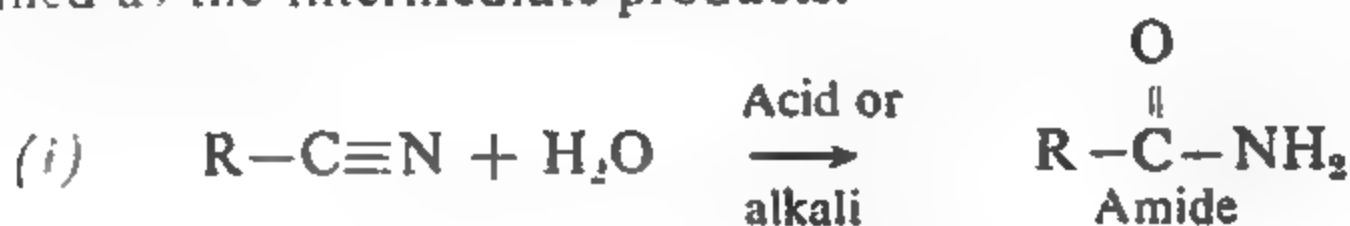
4. Industrially, alkyl cyanides are obtained by passing a mixture of the vapours of a carboxylic acid and ammonia over heated alumina.

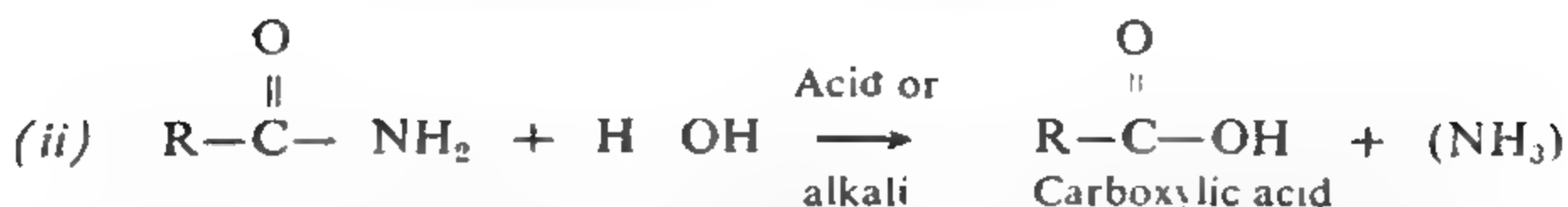


Physical Properties. The lower members (up to C_{14}) are colourless liquids with a strong characteristic sweet smell. The higher members are crystalline solids. They are moderately soluble in water but freely soluble in organic solvents. They are poisonous.

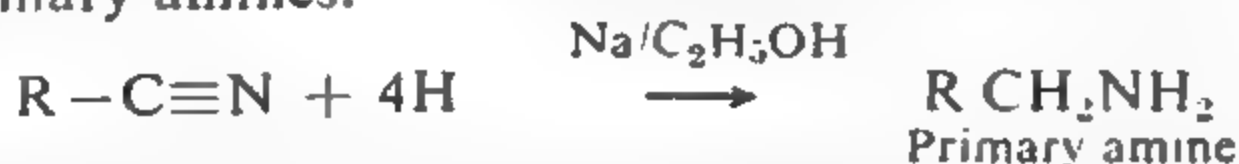
Chemical Properties. The important reactions of alkyl cyanides are :

(1) **Hydrolysis.** On boiling with an alkali or a dilute mineral acid, the cyanides are hydrolysed to give carboxylic acids. Amides are formed as the intermediate products.

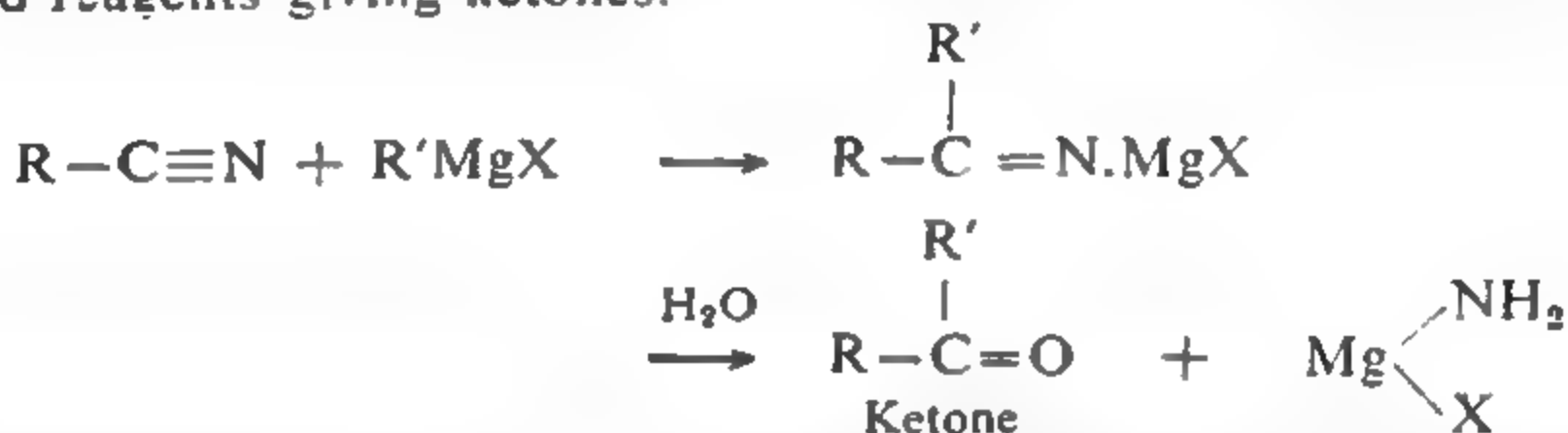




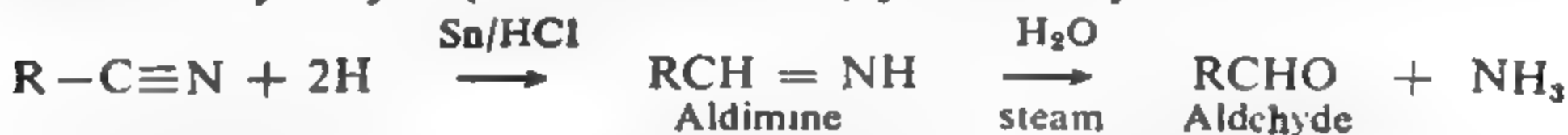
(2) **Reduction.** On reduction with lithium aluminium hydride or with sodium amalgam and alcohol (*Mendius reaction*), alkyl cyanides yield primary amines.



(3) **Reaction with Grignard reagents.** Alkyl cyanides react with Grignard reagents giving ketones.



(4) **Stephen's reaction.** Alkyl cyanides when reduced with tin and hydrochloric acid in ether or ethyl acetate solution give *aldimines* which on hydrolysis (steam distillation) yield aldehydes.



ALKYL ISOCYANIDES OR ACID ISONITRILES, CARBYLAMINES, R-NC

Preparation (1) Alkyl isocyanides are obtained by heating a primary amine with chloroform and alcoholic potash (*carbylamine reaction*).



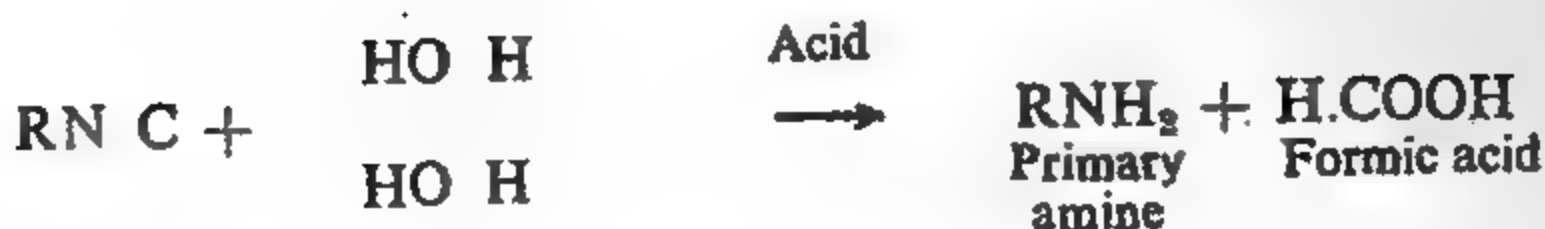
(2) Alkyl isocyanides may be obtained by the action of silver cyanide on alkyl halides. A small amount of the cyanide is also formed along with.



Physical Properties. Alkyl isocyanides are colourless, extremely unpleasant smelling, volatile liquids which are much more poisonous than the cyanides. They are only slightly soluble in water but are freely soluble in organic solvents.

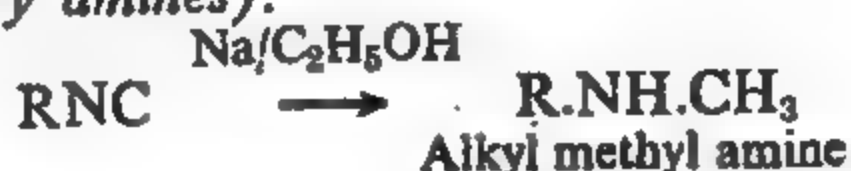
Chemical Properties. Alkyl isocyanides are highly reactive compounds and differ almost entirely from cyanides as illustrated below :

(1) **Hydrolysis.** Alkyl isocyanides are not hydrolysed by alkalis. With dilute mineral acids, however, they are hydrolysed to give *primary amines*. (*Distinction from cyanides which on hydrolysis by both acids and alkalis yield carboxylic acids*).



Isocyanide

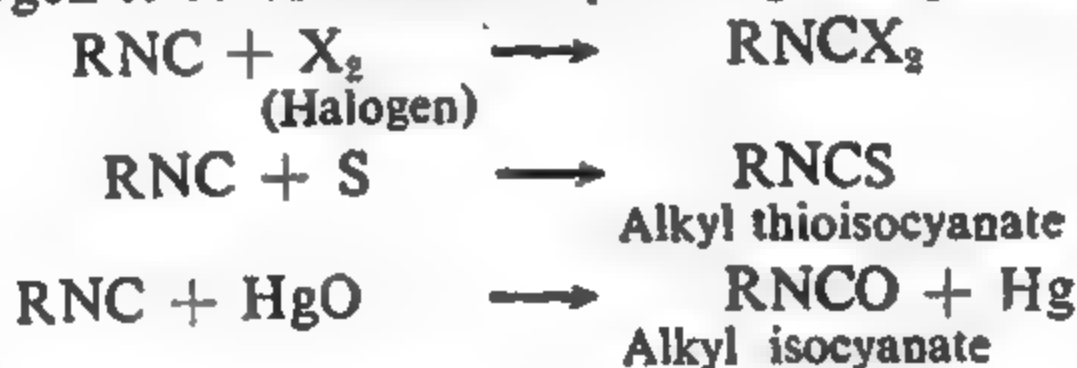
(2) **Reduction.** When reduced catalytically or by nascent hydrogen isocyanides give *secondary amines*. (*Distinction from cyanides which on reduction give primary amines*).



(3) **Isomerisation.** When heated at 250° for some time, they change into the isomeric cyanides showing thereby that cyanides are more stable than the isocyanides.



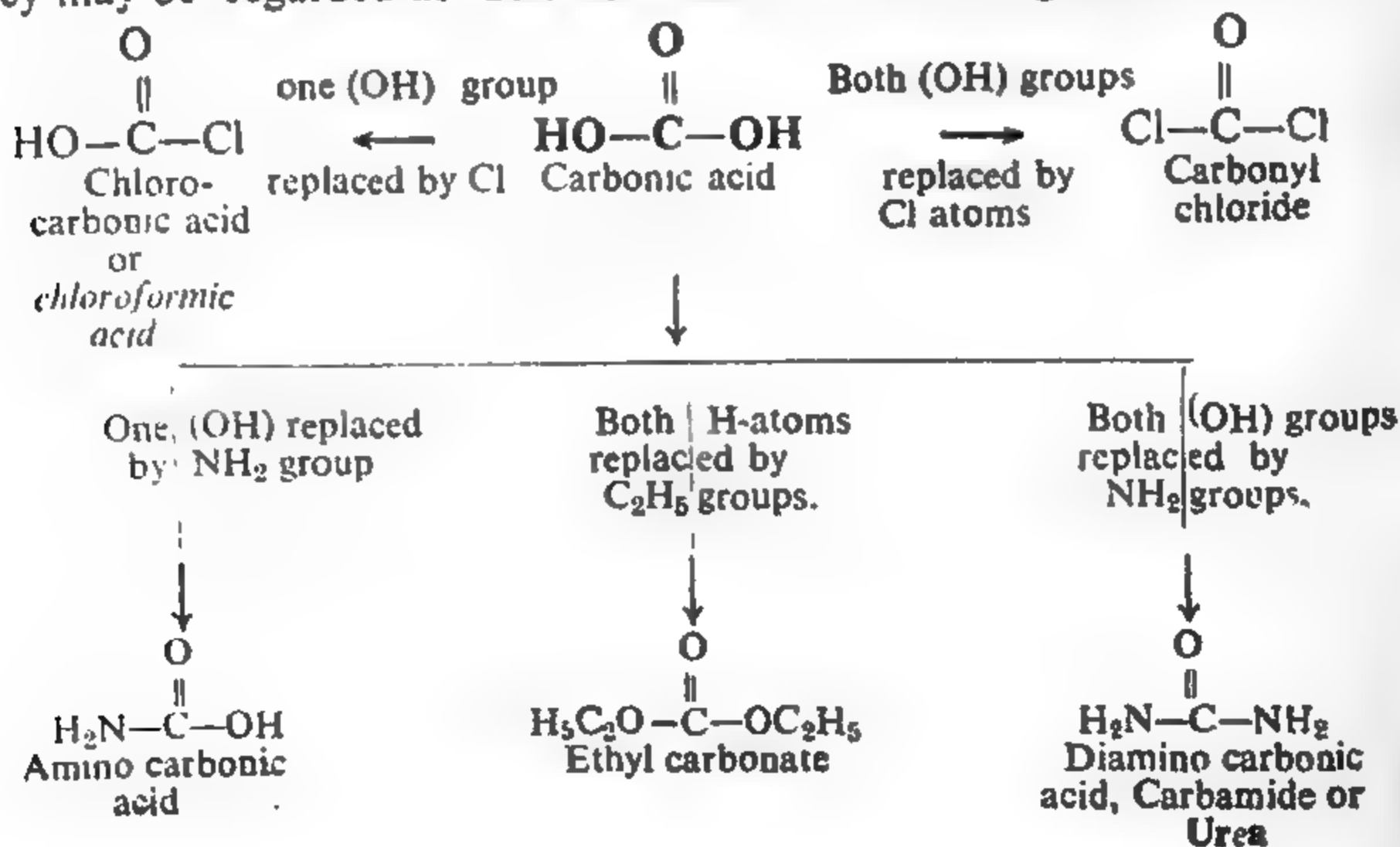
(4) **Addition Reactions.** Alkyl isocyanides add on halogens, sulphur and oxygen to form the corresponding compounds.



DERIVATIVES OF CARBONIC ACID

Carbonic acid is unstable and cannot be isolated in the free state. It, however, forms a number of derivatives which are stable and highly useful.

The various derivatives of carbonic acid and the manner in which they may be regarded as derived from the latter are given below :

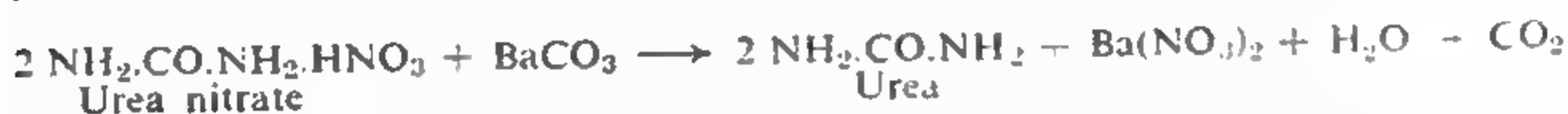


The most important derivative is **urea** which has been described, in details, below :

UREA, CARBAMIDE, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}_2$

Urea was isolated for the first time in 1773 by Roulle from urine and hence the name. It is formed in man and mammals as a result of decomposition of proteins and is excreted in urine. Urea was the first organic compound synthesised from inorganic substances (Wohler, 1828).

Preparation (1) From urine. The concentrated urine is treated with concentrated nitric acid when urea nitrate, $\text{NH}_2\text{CO NH}_2\text{HNO}_3$, separates out in the form of a crystalline precipitate. This is dissolved in water and treated with barium carbonate when urea is liberated.

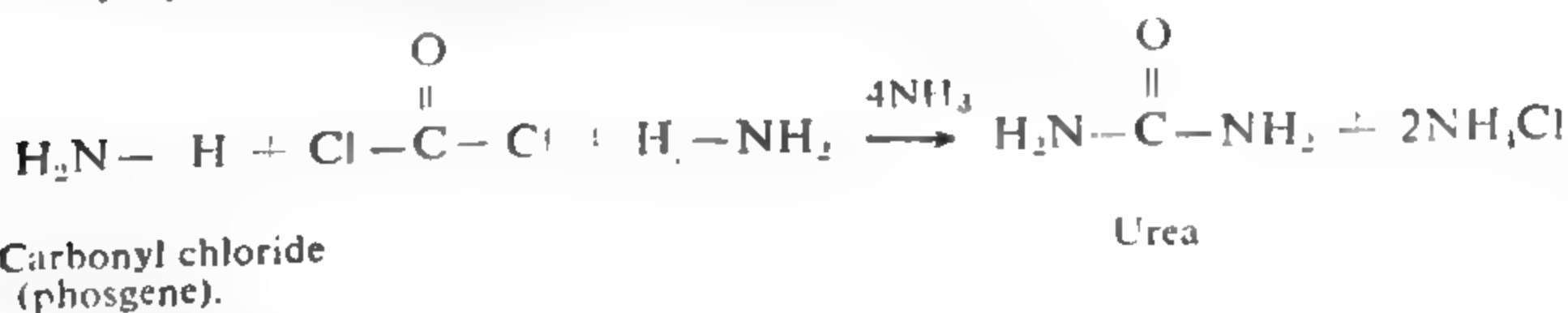


Any excess of barium carbonate is filtered off and the solution evaporated to dryness. Pure urea is extracted by alcohol in which barium nitrate is not soluble.

(2) **From ammonium cyanate.** Urea may be conveniently prepared in the laboratory by *Wohler's method*, that is, by evaporating an aqueous solution of potassium cyanate and ammonium sulphate, when the ammonium cyanate formed undergoes molecular rearrangement to give urea.



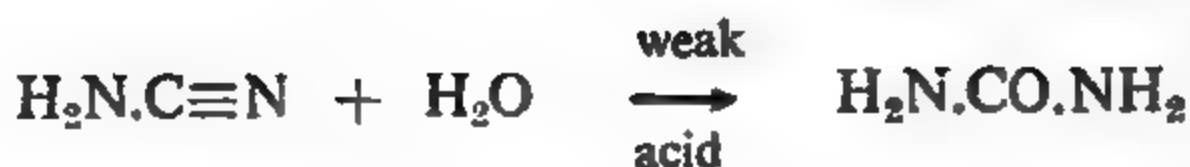
(3) **From carbonyl chloride.** Urea may also be prepared in the laboratory by interacting carbonyl chloride with ammonia.



(4) **From carbon dioxide and ammonia.** Urea is now prepared industrially by the interaction of liquid ammonia and liquid carbon dioxide under pressure. The ammonium carbamate produced is heated at 130-150° under a pressure of about 35 atmospheres to lose a molecule of water giving urea.



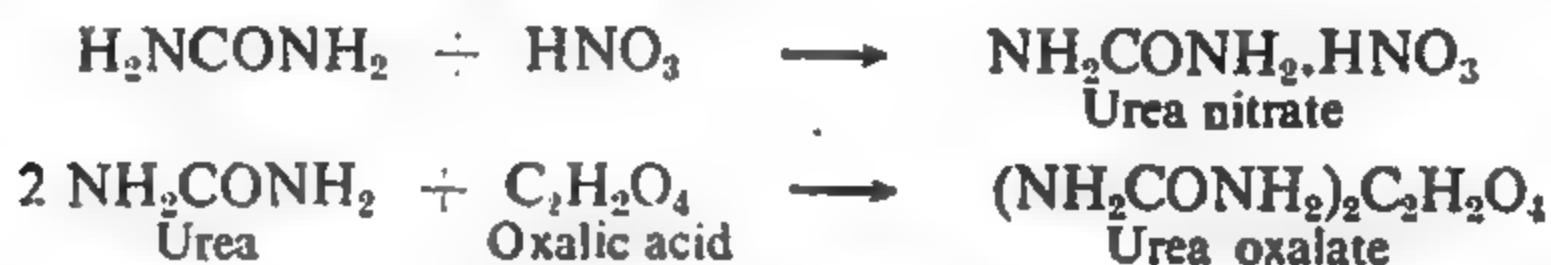
Previously urea was prepared by partial hydrolysis of cyanamide in a weakly acidic solution.



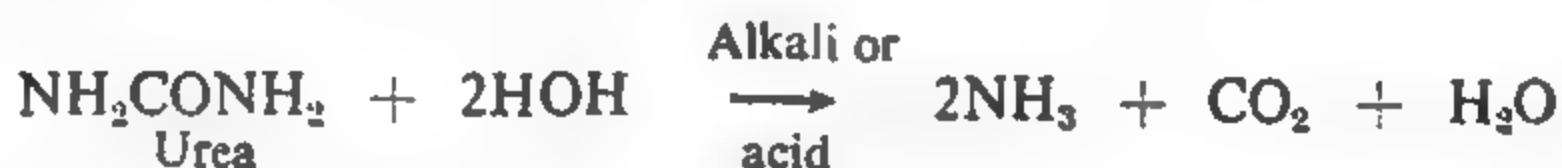
Physical Properties. Urea is a white crystalline solid, melting at 132° . It is soluble in water and alcohol but is insoluble in ether.

Chemical Properties. Urea essentially exhibits the character of an amide, though in certain aspects it behaves like amines. The more important reactions of urea are described below :

(1) **Basic nature.** Urea behaves as a *monoacid base* and forms crystalline salts with strong acids (*cf.* amines). The most important salts are *urea nitrate* and *urea oxalate*.

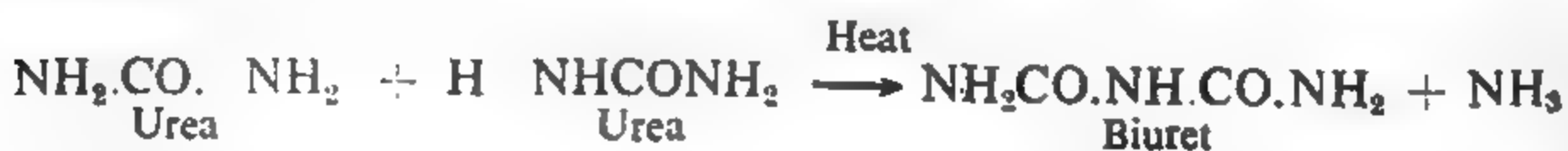


(2) **Hydrolysis.** Urea, like other amides, is easily hydrolysed when heated with an alkali or a dilute mineral acid to give ammonia and carbon dioxide.



The above hydrolytic decomposition is also carried out *quantitatively* by an enzyme, *urease*, present in soyabeans. The ammonia evolved can be estimated volumetrically and hence this reaction is used for the estimation of urea.

(3) **Action of heat.** Urea, when heated gently, loses ammonia to form *biuret*.

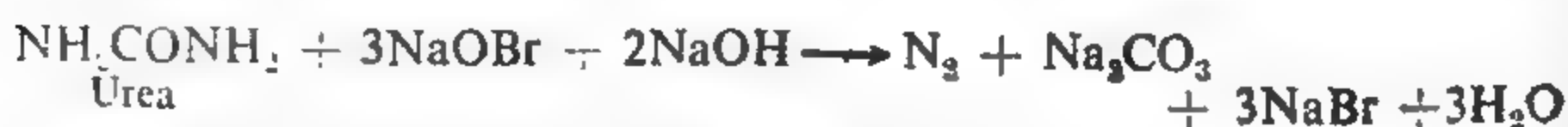


Biuret gives violet colouration on the addition of small amounts of dilute sodium hydroxide and copper sulphate solutions (*biuret test*).

(4) **Action of nitrous acid.** Urea is decomposed into gaseous nitrogen and carbon dioxide on treatment with nitrous acid.



(5) **Action of alkaline hypobromite.** On treatment with alkaline solution of sodium or potassium hypobromite, urea is again decomposed into gaseous nitrogen.

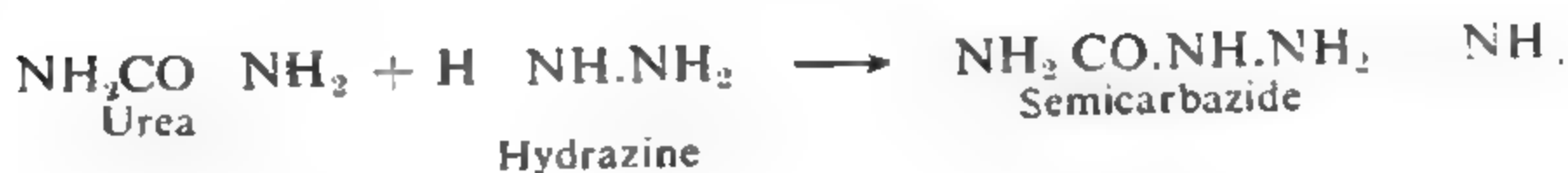


This reaction is used in the estimation of urea.

(6) **Action of acid chlorides and acid anhydrides.** Urea reacts with acid chlorides and acid anhydrides to give acetyl derivatives known as ureides (*cf.* amines).

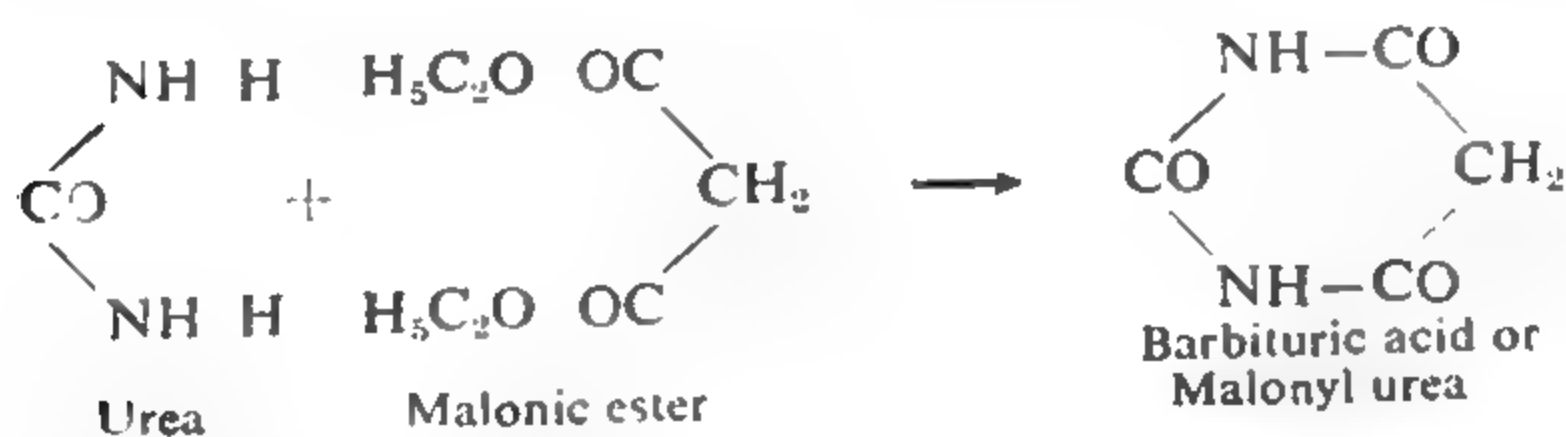


(7) **Action with hydrazine.** Urea reacts with hydrazine (NH_2NH_2) to form semicarbazide.



Semicarbazide is an important reagent used for identification and separation of sugars.

(8) **Action with malonic ester.** Urea reacts with malonic ester (diethyl malonate) to form barbituric acid or malonyl urea.



Barbituric acid and its derivatives are important hypnotics and sedatives and have been frequently used as such in medicine.

Uses. Urea is used :

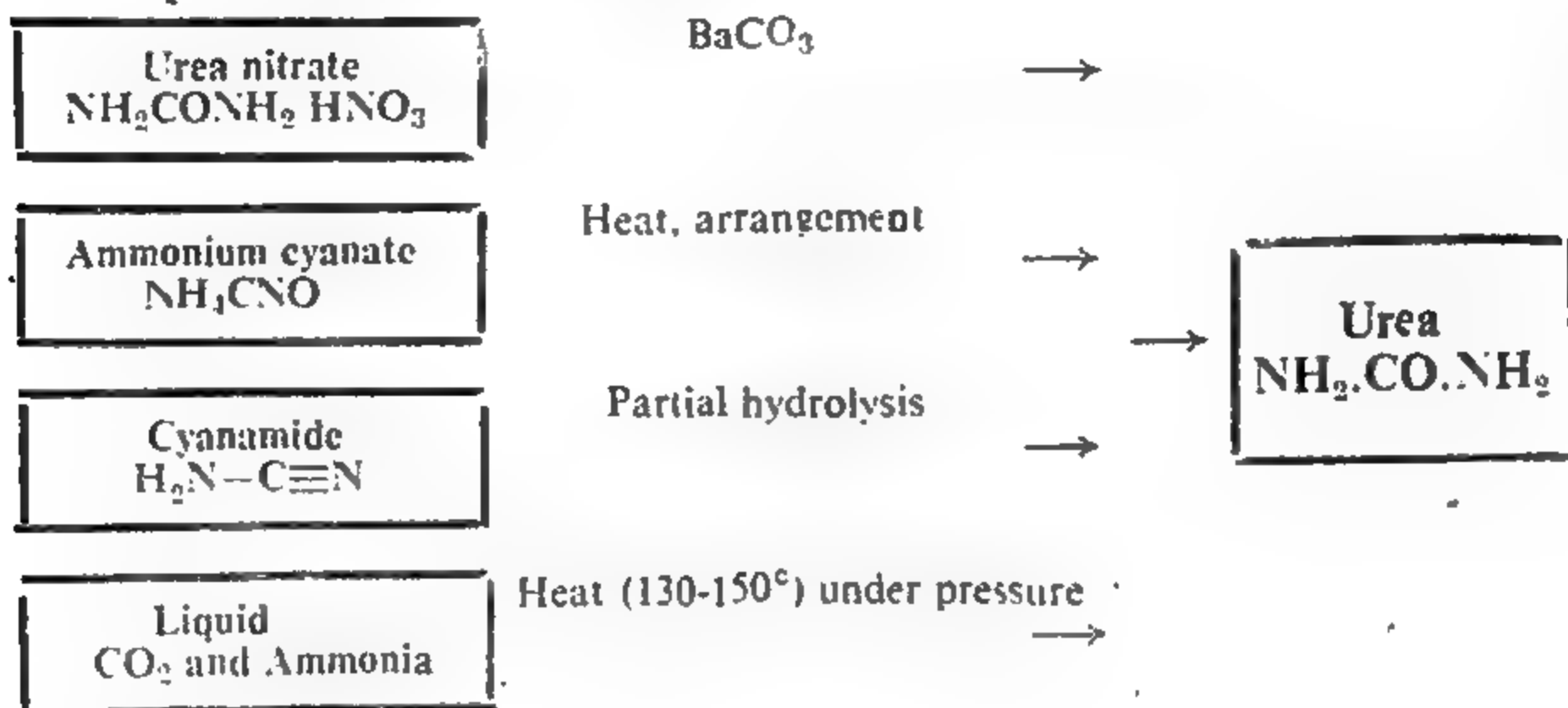
- (i) Extensively as a fertilizer.
- (ii) In the manufacture of formaldehyde-urea plastics.
- (iii) In the preparation of drugs and hypnotics.
- (iv) As a stabiliser for nitrocellulose explosives.

Tests. (1) Urea can be identified by the *biuret* test.

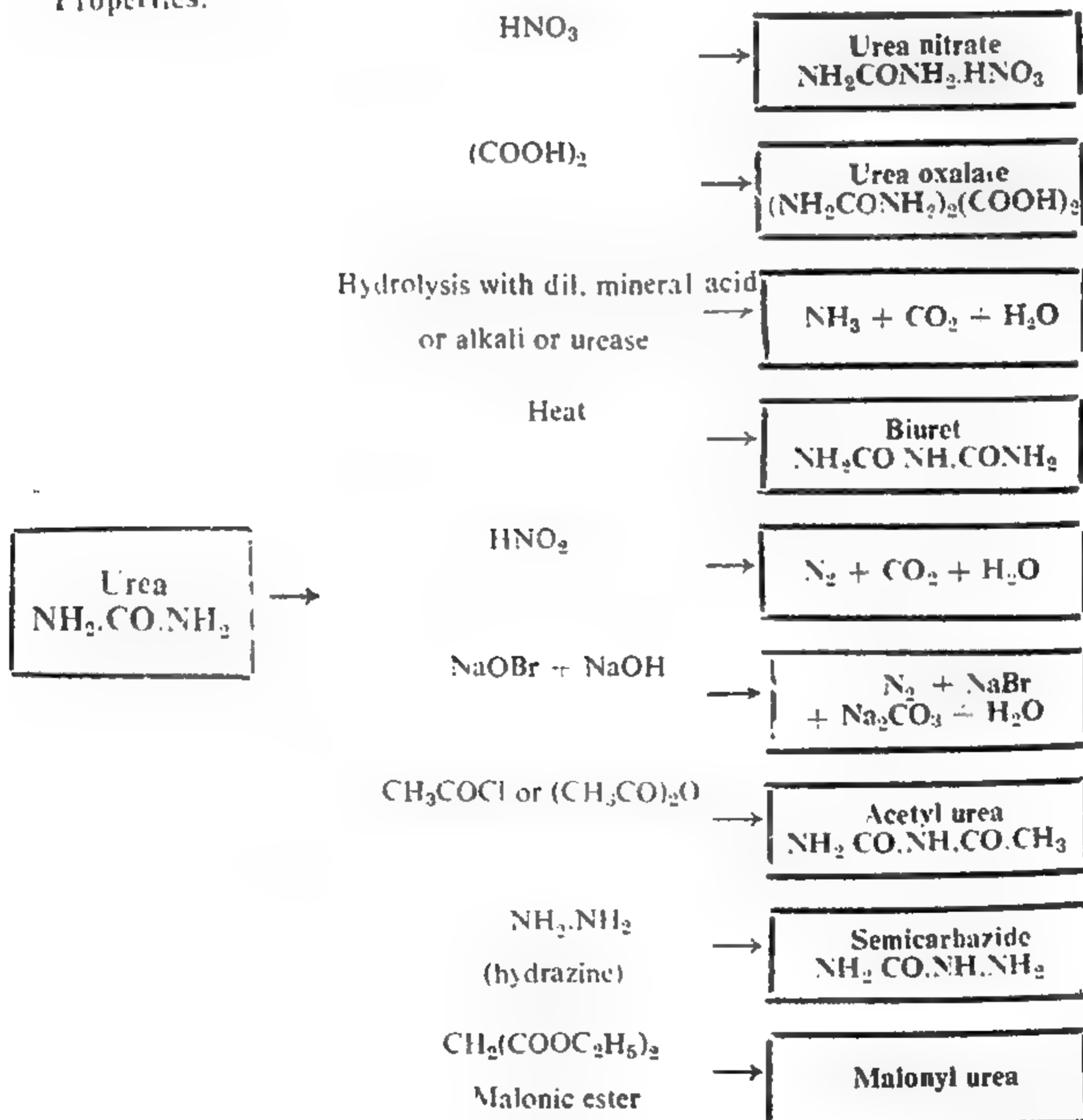
(2) On adding sodium nitrite to a solution of urea, containing dilute hydrochloric acid, nitrogen gas is given out.

SUMMARY OF TYPICAL MEMBER PREPARATION AND PROPERTIES OF UREA

Preparation.



Properties.



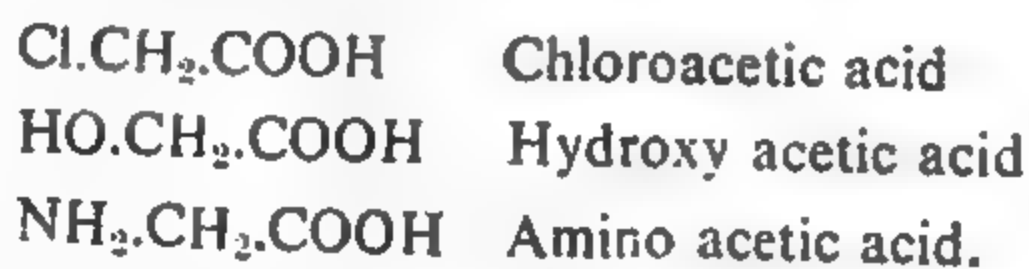
QUESTIONS

1. Give the methods of preparation and properties of ethyl nitrate.
2. How can ethyl nitrate be prepared? Describe its important reactions and uses.
3. Describe the preparation of ethyl hydrogen sulphate. How can it be converted into (i) ethyl alcohol (ii) diethyl ether (iii) ethylene (iv) diethyl sulphate and (v) ethyl bromide?
4. Describe the methods of preparation, properties and uses of dimethyl sulphate.
5. How can ethyl cyanide be prepared? Describe its typical reactions.
6. How can ethyl isocyanide be prepared? Describe its typical reactions.
7. What are nitriles and isonitriles? How would you distinguish between them?
8. Describe the various methods for the preparation of urea. Give its important properties and uses.
9. How is carbamide prepared (i) in laboratory (ii) on a commercial scale? Describe the important properties and uses of this compound.
10. Urea reacts with nitrous acid to give CO_2 , H_2O and N_2 . Taking this reaction as a quantitative one, calculate the weight of CO_2 and H_2O and the volume of N_2 under normal conditions obtained from 0.2 gm of urea.
(C = 12, H = 1, N = 14, O = 16) (Panjab Inter 1956)
(Ans $\text{CO}_2 = 0.146 \text{ gm.}$, $\text{H}_2\text{O} = 0.18 \text{ gm.}$, $\text{N}_2 = 149.3 \text{ c.c.}$)
11. Give the occurrence, preparation, important properties and uses of urea. (Panjab Inter 1956, 54)
12. Write a concise note on the chemistry of urea (Panjab Inter 1953)
How is urea prepared in the laboratory and on industrial scale? Describe some important uses of the compound. How does it react with
(a) HNO_3 (b) NaOH (c) Br_2 and KOH ?

CHAPTER XXXVII

SUBSTITUTED CARBOXYLIC ACIDS

The substituted carboxylic acids are derived from carboxylic acids by the substitution of one or more hydrogen atoms of the alkyl group by other atoms or groups such as $-\text{Cl}$, $-\text{OH}$, $-\text{NH}_2$ etc. Thus, there are: *halogenated acids*, *hydroxy acids*, *amino acids*, etc. They are usually named after the carboxylic acid from which they are derived. For instance, the derivatives of acetic acid will be



In order to name the higher members, the carbon atoms are usually designated as α , β , γ , δ .. starting from the carbon atom carrying the carboxylic group and the position of the substituent is indicated accordingly. For example,

$\begin{matrix} \gamma & \beta & \alpha \\ \text{CH}_3 & \text{CHOH} & \text{CH}_2 \cdot \text{COOH} \end{matrix}$ is named as β -hydroxy butyric acid
and $\text{CH}_3\text{CH}_2\text{CHCl} \cdot \text{COOH}$ is named as α -chloro butyric acid.

Evidently, the substituted acids are compounds containing two functional groups and hence they will give reactions characteristic of both the groups, viz., the carboxyl group and the respective substituent group.

Some of the typical members of the substituted acids have been described below.

CHLOROACETIC ACID, $\text{CH}_2\text{Cl} \cdot \text{COOH}$

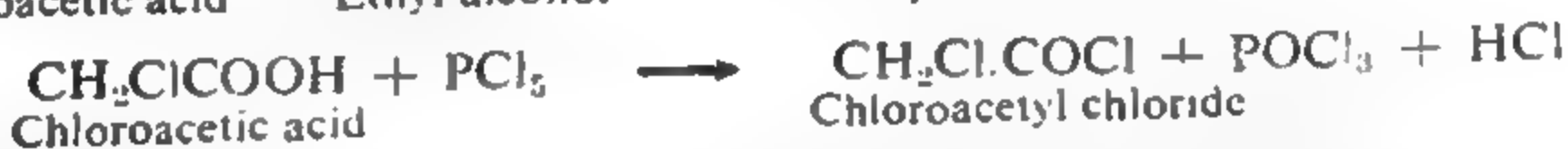
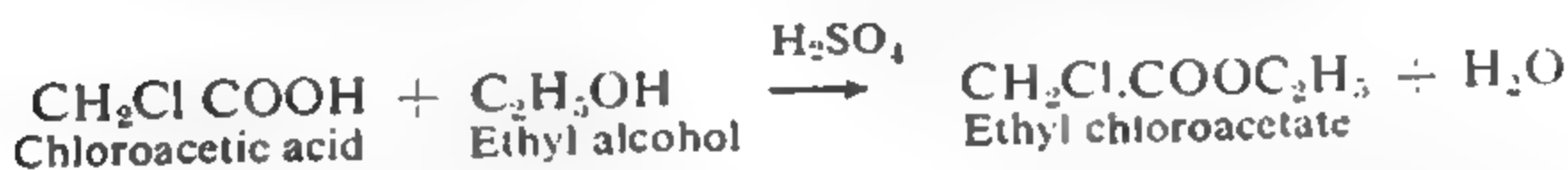
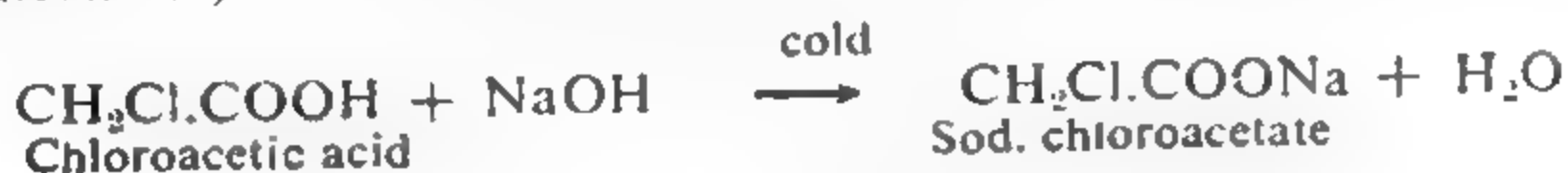
Preparation. (1) It is prepared on a commercial scale by passing chlorine into glacial acetic acid at 100° in the presence of red phosphorus, (catalyst).



Physical Properties. Chloroacetic acid is a colourless, crystalline solid (m.p. 62°), soluble in water. It is a much stronger acid than acetic acid and has a strong corrosive action on the skin.

Chemical Properties. Chloroacetic acid gives the reactions of a carboxyl group as well as of an active chlorine atom.

Reactions of a carboxyl group. Chloroacetic acid gives the usual reactions of a $-\text{COOH}$ group, such as formation of *salts with alkalis*; *esters with alcohols*; *acid chlorides with phosphorus halides*, etc. For example,



Reactions of chlorine atom. The chlorine atom can be readily replaced (as in alkyl halides) by other atoms or groups by appropriate treatments. For example,

(1) On boiling with water, the *Cl-atom* is replaced by (*OH*) group.



On boiling with aqueous alkali, the end product will be the sodium salt of glycollic acid.

(2) On treatment with *alcoholic ammonia*, the *Cl-atom* is replaced by $-\text{NH}_2$ group.



(3) On boiling with aqueous potassium cyanide, the *Cl-atom* is replaced by the *cyanide group*.



(4) On treatment with potassium iodide or sodium iodide, the *Cl-atom* is replaced by the *iodine atom*.



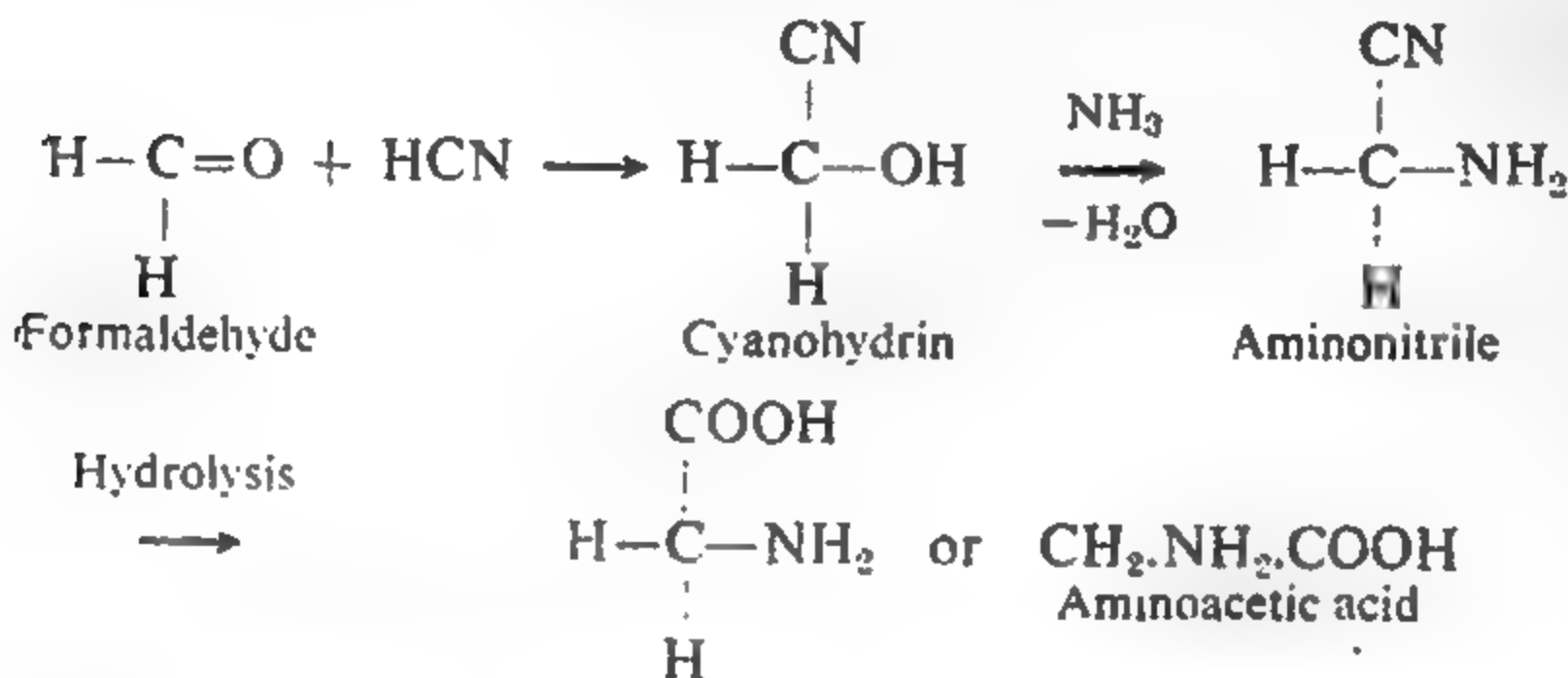
Uses (1) Chloroacetic acid is used as a synthetic reagent for the preparation of hydroxy and amino acids, indigo, etc. It is also used as a sterilizing agent.

AMINOACETIC ACID, $\text{CH}_2\text{NH}_2\text{COOH}$, GLYCINE

Preparation. (1) Amino acetic acid is prepared by the action of alcoholic ammonia solution on chloroacetic acid.



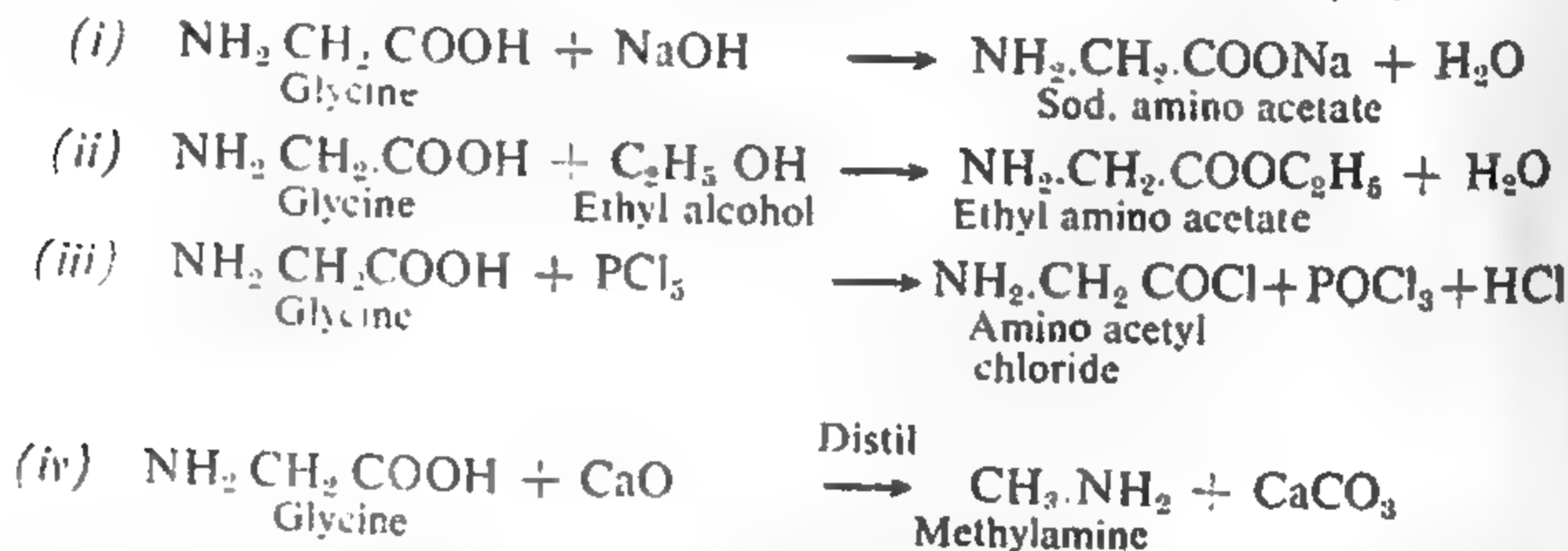
(2) It may also be obtained from formaldehyde as below :



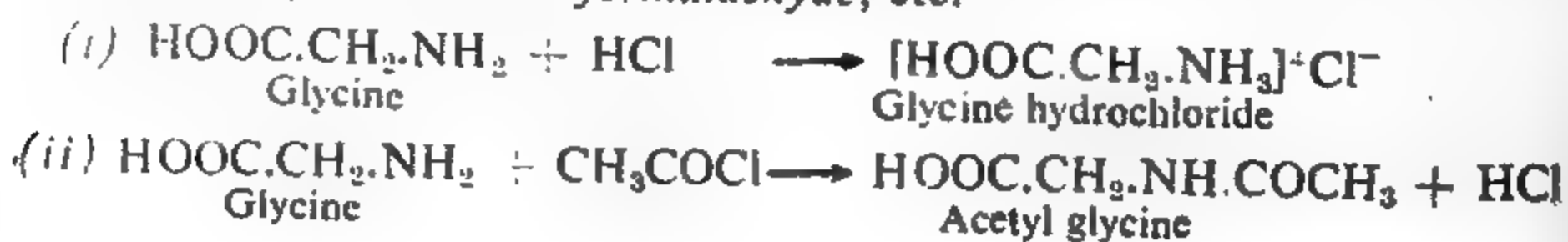
Physical Properties Aminoacetic acid is a white crystalline solid (m.p. 235°). highly soluble in water but practically insoluble in alcohol and ether. It has a sweet taste, hence the name *glycine* (*Greek, glycos* means sweet.)

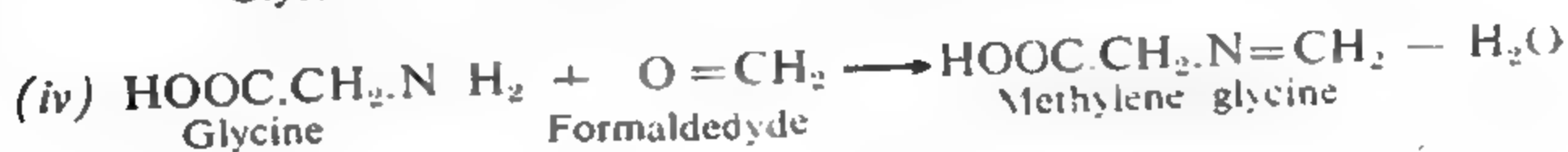
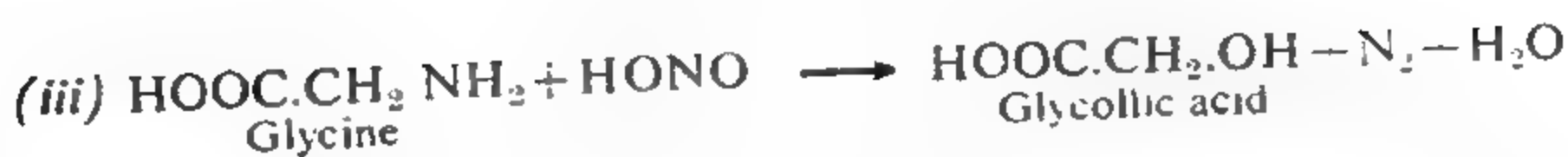
Chemical Properties Glycine gives reactions of both carboxyl and amino groups.

Reactions of carboxyl group. Glycine gives the usual reactions of a carboxyl group, such as *formation of salts with alkalies ; esters with alcohols ; acid chlorides with phosphorus halides*, etc. For example,

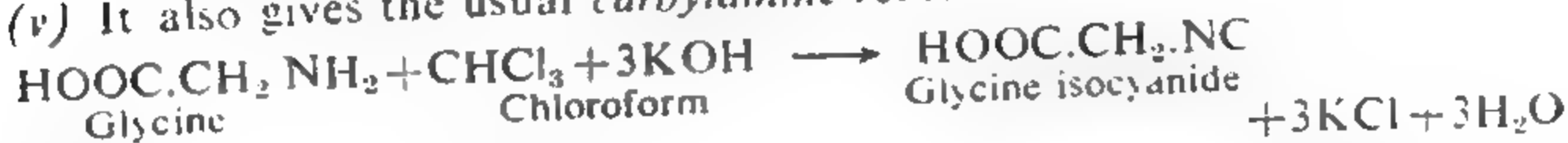


Reactions of amino group. Glycine also gives the usual reactions of an amino group such as *formation of salts with strong acids ; acetyl derivatives with acetyl chloride ; hydroxy derivatives with nitrous acid and condensation products with formaldehyde*, etc.





(v) It also gives the usual *carbylamine reaction*.



Uses. Glycine is used for the manufacture of resins and varnishes. It is also used as a medicine in certain muscular diseases. It eliminates toxic substances from our body, for instance, benzoic acid is removed as benzoyl glycine.

HYDROXY ACETIC ACID, *Glycollic Acid*, $\text{CH}_2(\text{OH})\text{COOH}$

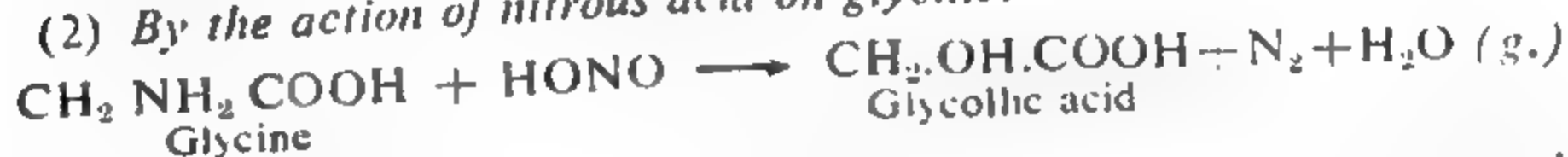
Glycollic acid is the simplest hydroxy acid.

Preparation. Glycollic acid may be prepared by the following methods :

(1) *By boiling an aqueous solution of chloroacetic acid with water.*



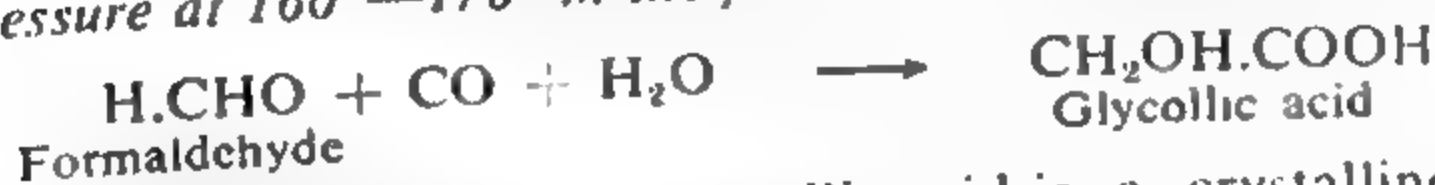
(2) *By the action of nitrous acid on glycine.*



(3) *By the electrolytic reduction of oxalic acid (commercial preparation).*



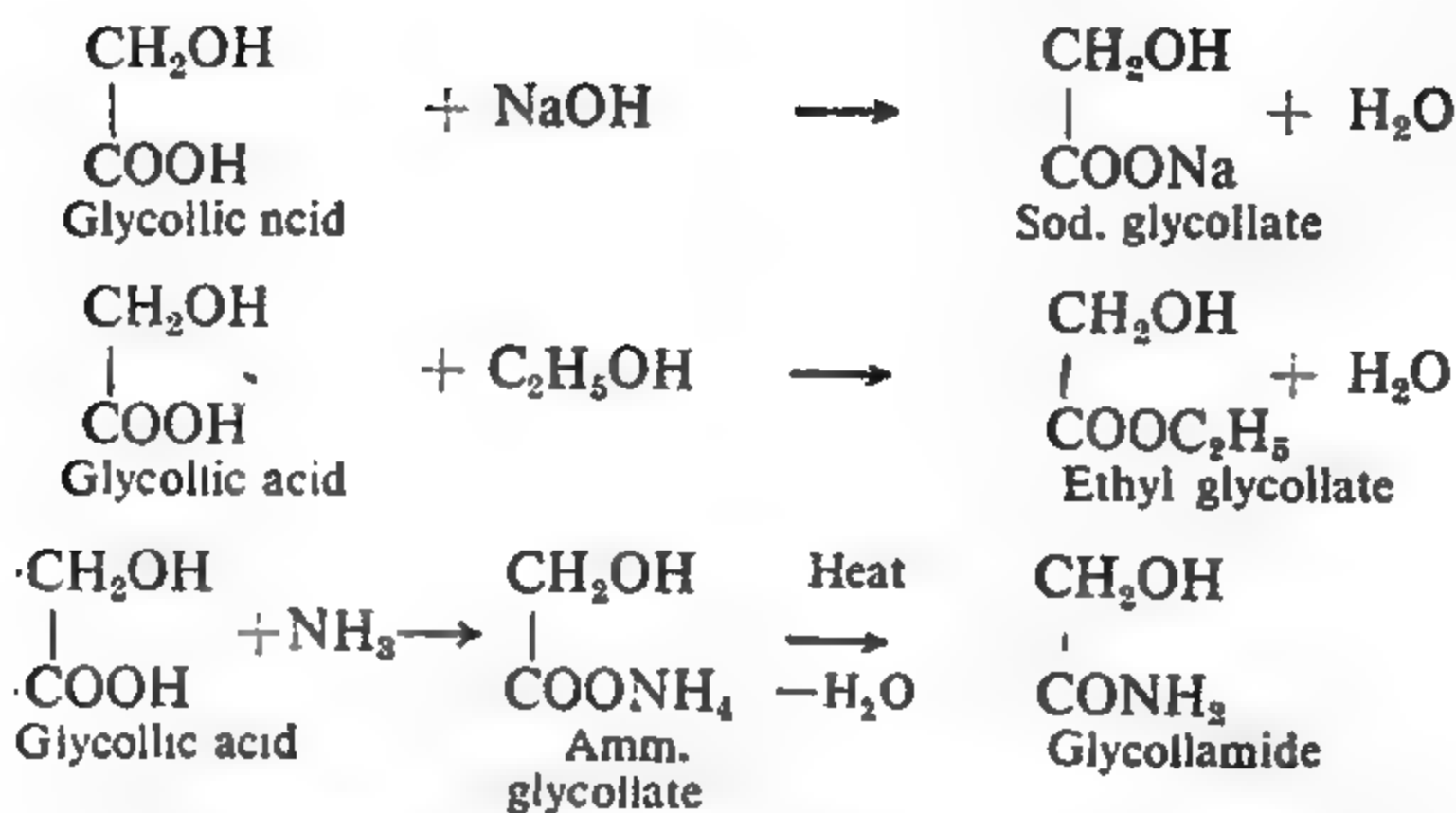
(4) *By heating formaldehyde with carbon monoxide and water under pressure at $160^\circ - 170^\circ$ in the presence of a catalyst (commercial method).*



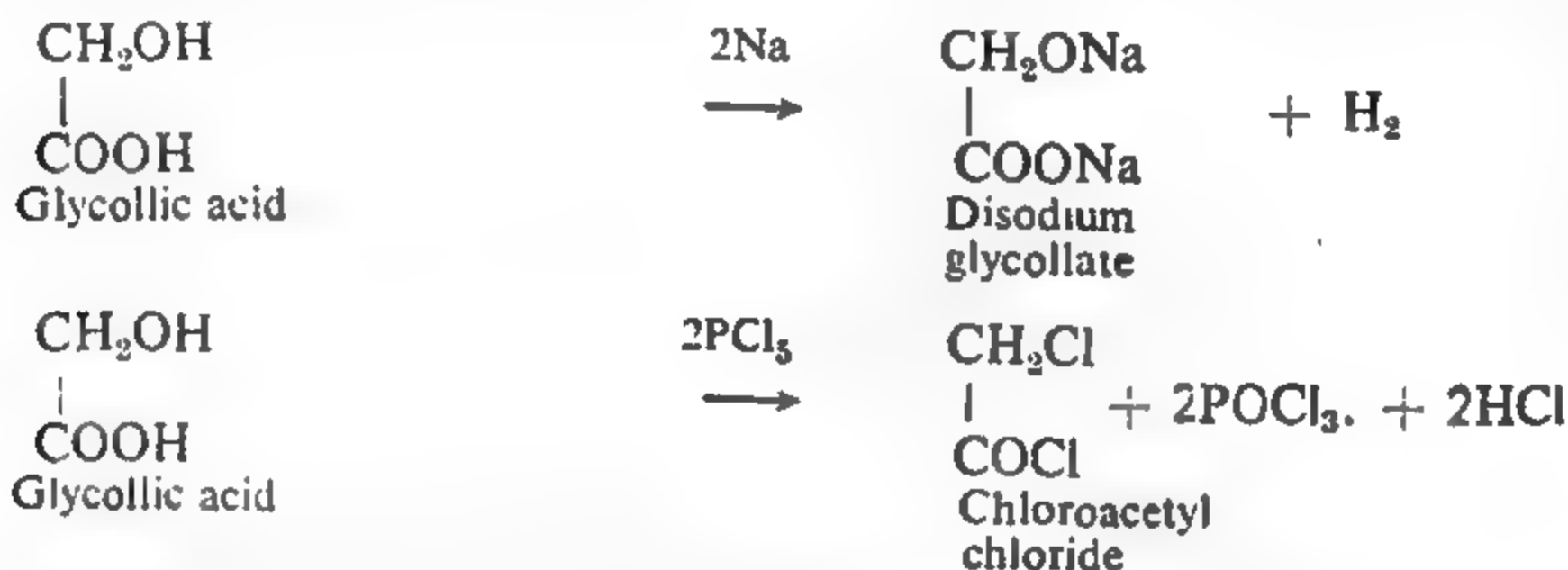
Physical Properties. Glycollic acid is a crystalline substance (m.p. 79°), hygroscopic and readily soluble in water, ethanol and ether.

Chemical Properties. Glycollic acid, $\text{CH}_2(\text{OH})\text{COOH}$, contains a carboxyl as well as a primary alcoholic group, hence it combines the properties of both.

(1) It forms salts with alkalies, esters with alcohols, and amides with ammonia.



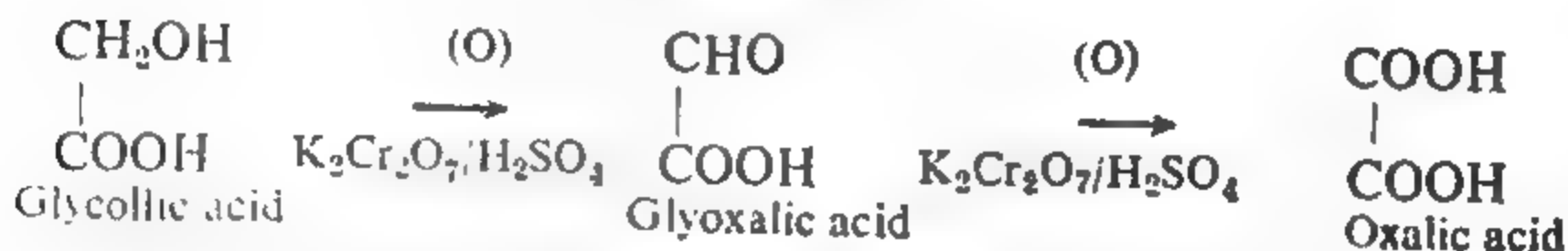
(2) It reacts with Na metal and with PCl_5 , when both the functional groups are attacked.



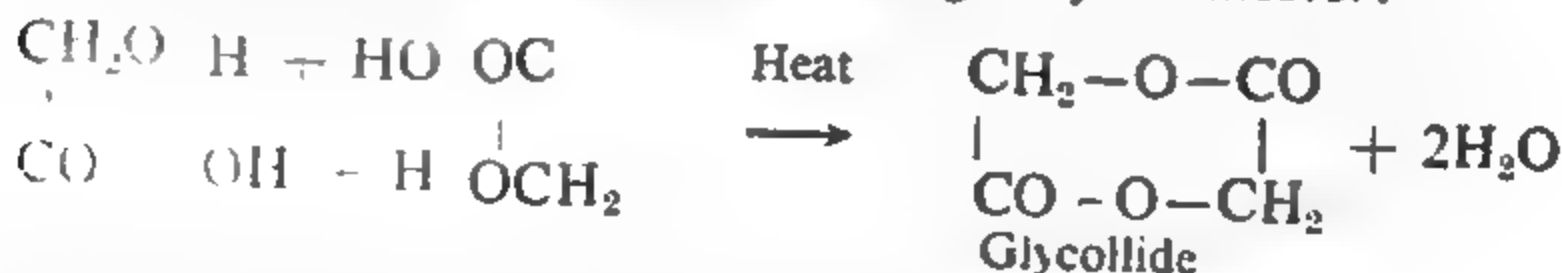
(3) It reacts with acetyl chloride giving the *acetyl derivative*.



(4) On oxidation, it gives oxalic acid.



(5) On heating, it loses water, forming a *cyclic diester*.



LACTIC ACID, α -Hydroxy Propionic Acid $\text{CH}_3\text{.CHOH.COOH}$.

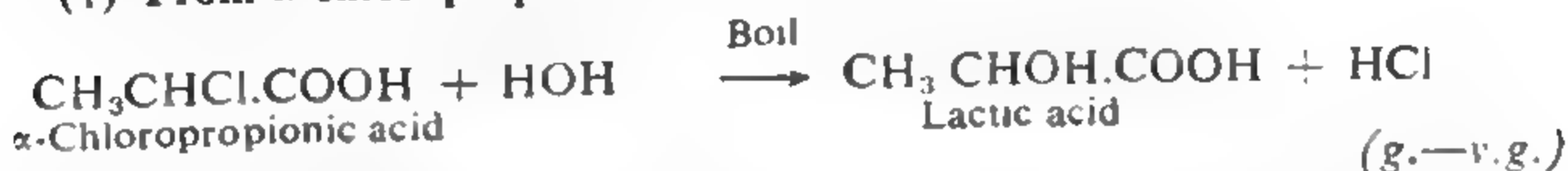
Lactic acid is present in sour milk where it is produced by the fermentation of milk sugar (lactose) by the bacteria known as *lactic bacilli*.



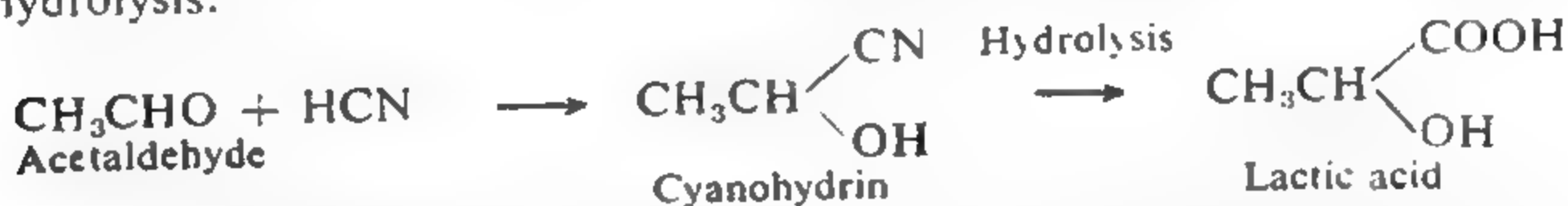
Hence, the name lactic acid (Latin, *lac* means milk).

Preparation. Lactic acid is prepared :

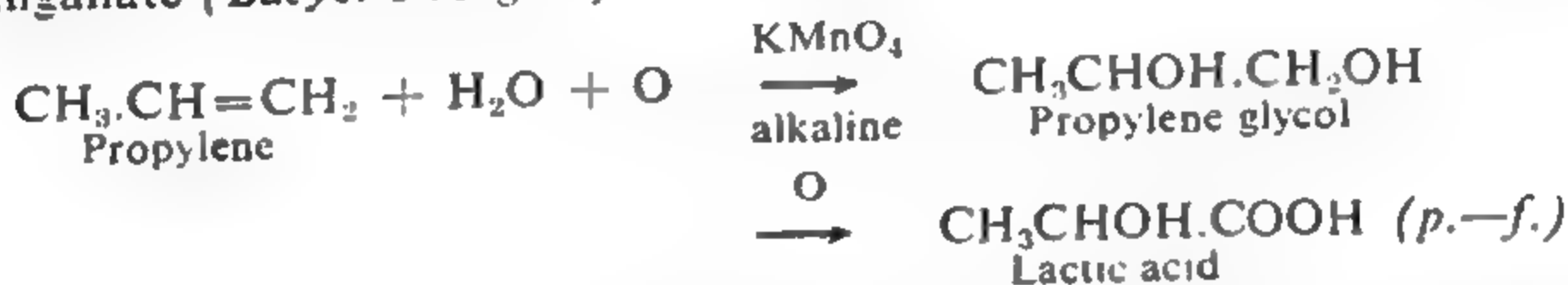
(1) From α -chloropropionic acid. By boiling with water.



(2) From acetaldehyde By interaction with HCN and subsequent hydrolysis.



(3) From propylene By oxidation with cold dilute alkaline permanganate (*Baeyer's reagent*).



(4) From sugars. Lactic acid is prepared industrially by the fermentation of cane-sugar by *lacto bacillus* present in sour milk. The optimum conditions are (i) neutral solution and (ii) 35—37° temperature.



Molasses, containing about 50 per cent of cane-sugar, is diluted with water and treated with sour milk at about 37°, in the presence of powdered chalk (calcium carbonate). The lactic acid formed during fermentation combines with the chalk forming calcium lactate, which being sparingly soluble settles down. When fermentation is complete, the calcium lactate is filtered and treated with dilute sulphuric acid to liberate lactic acid which is recovered from the filtrate by vacuum distillation.

Physical Properties. Pure lactic acid is a colourless crystalline solid, melting at 18°. Because of its extremely deliquescent nature and low melting point, it is generally present in the form of a thick syrupy liquid. It is readily miscible with water, ethanol and ether.

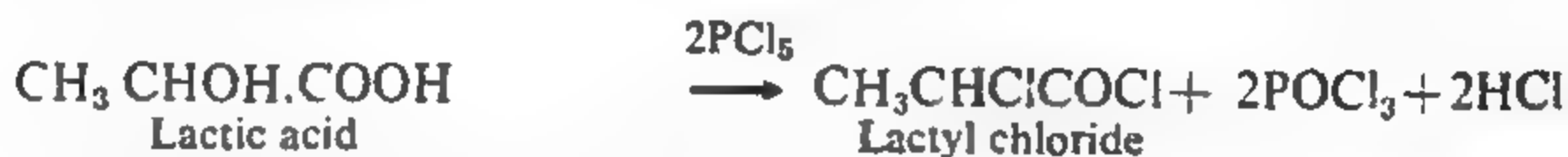
Chemical Properties. Lactic acid contains a carboxyl as well as a secondary alcoholic group, hence it combines the properties of both.

(1) It forms salt with alkalis and esters with alcohols.

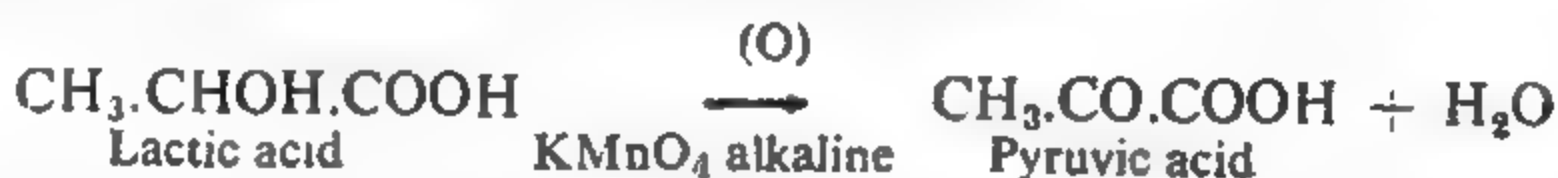




(2) With phosphorus pentachloride, both the (OH) and the —COOH groups are attacked.



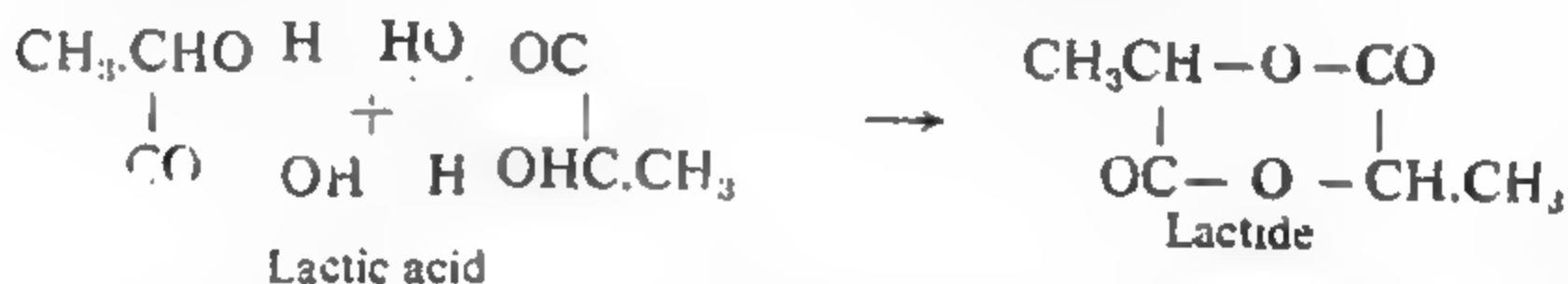
(3) On oxidation with hot alkaline permanganate, the secondary alcoholic group is oxidised to the *ketonic group*.



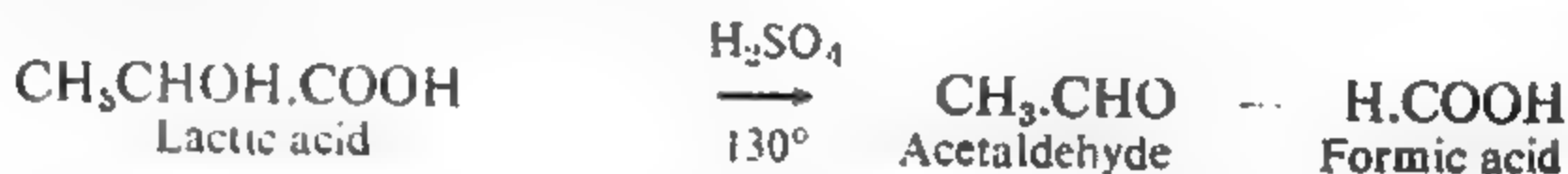
(4) On reduction with hydriodic acid, the —CHOH group is reduced to —CH₂.



(5) On heating alone, it loses water, giving a cyclic diester.



(6) On heating with dilute sulphuric acid at 130°, it decomposes to give *acetaldehyde* and *formic acid*.



(7) On warming with iodine and alkali, it gives iodoform (*Iodoform reaction*).

Uses. Lactic acid is used as a mordant in dyeing wool ; for deliming of hides in tanning and as a medicine in the form of calcium lactate and iron lactate. Its ethyl and butyl esters are used as solvents.

TARTARIC ACID, (Dihydroxy Succinic Acid).



It occurs in the free state and as potassium hydrogen tartrate in tamarind (*'imli'*) and grapes.

Preparation.

Industrially, tartaric acid is obtained from the potassium hydrogen tartrate which separates out in the form of a reddish-brown crystalline mass during the fermentation

of grape juice to wine. This brown mass is known as argol which on recrystallisation gives a white pure substance known as cream of tartar. This is dissolved in water and neutralised by calcium hydroxide when a mixture of calcium tartrate (insoluble) and potassium tartrate (soluble) is obtained.



The calcium tartrate is separated by filtration and the filtrate containing potassium tartrate is treated with calcium chloride to get a precipitate of calcium tartrate which is isolated.

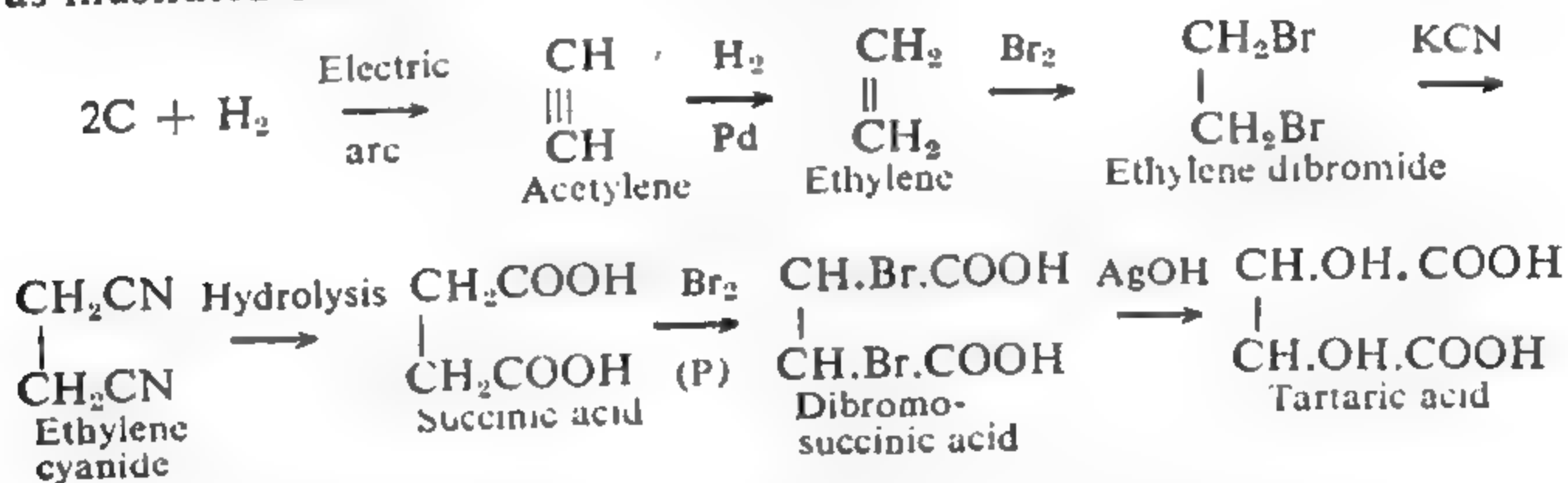


The total lot of calcium tartrate is then treated with calculated amount of sulphuric acid to liberate tartaric acid.



The calcium sulphate is removed by filtration and the tartaric acid left in solution is crystallised out.

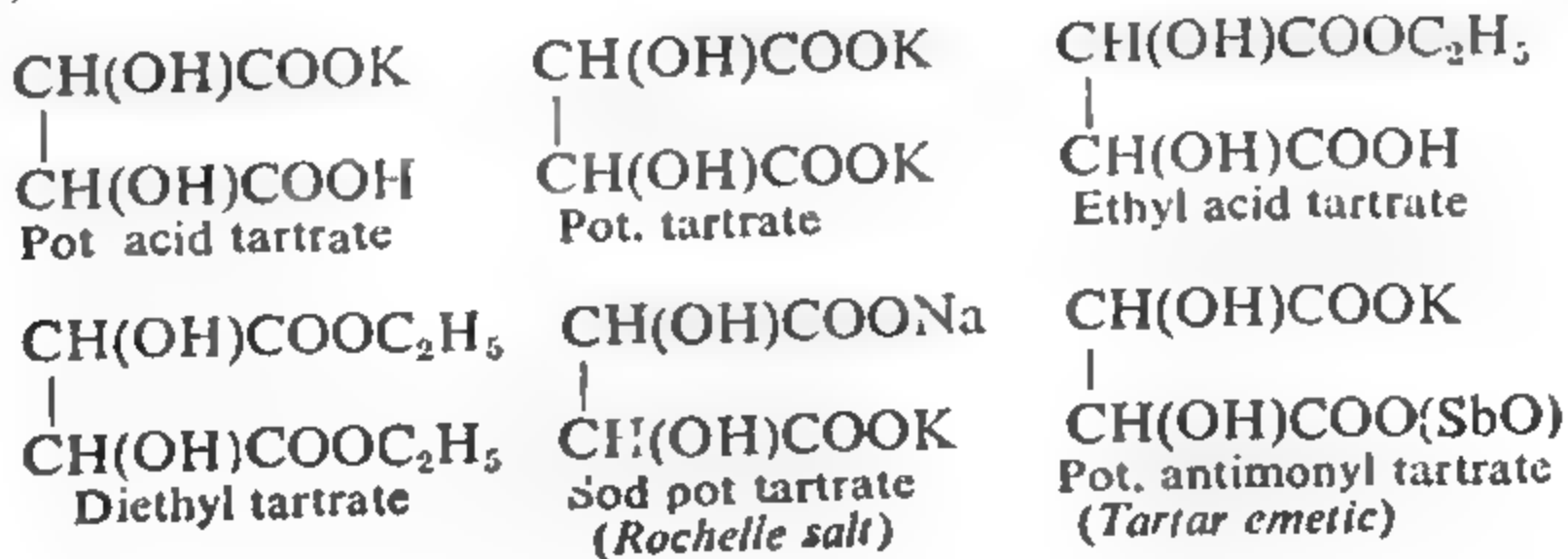
Synthesis Tartaric acid can be synthesised from carbon and hydrogen as illustrated below :



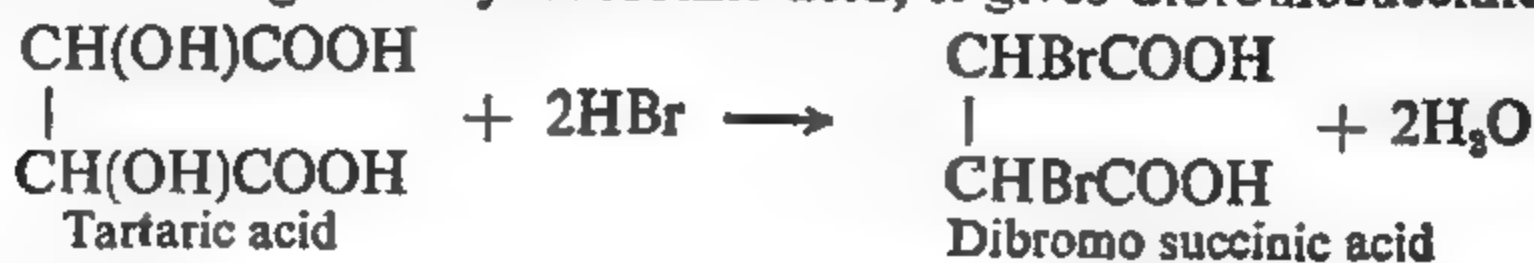
This complete synthesis of tartaric acid also proves its structure.

Physical Properties. Tartaric acid crystallises in the form of large monoclinic prisms melting at 206° . It is readily soluble in water but insoluble in ether.

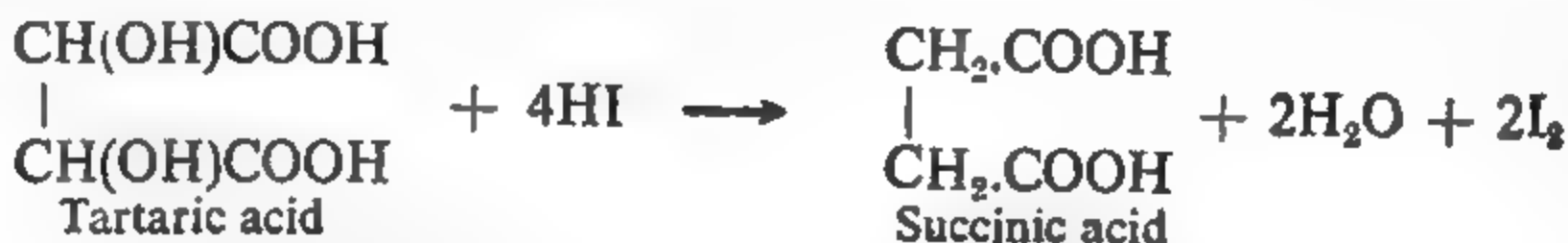
Chemical Properties. (1) Tartaric acid is a dibasic acid and it forms two series of salts with alkalies and two series of esters with alcohols. For example,



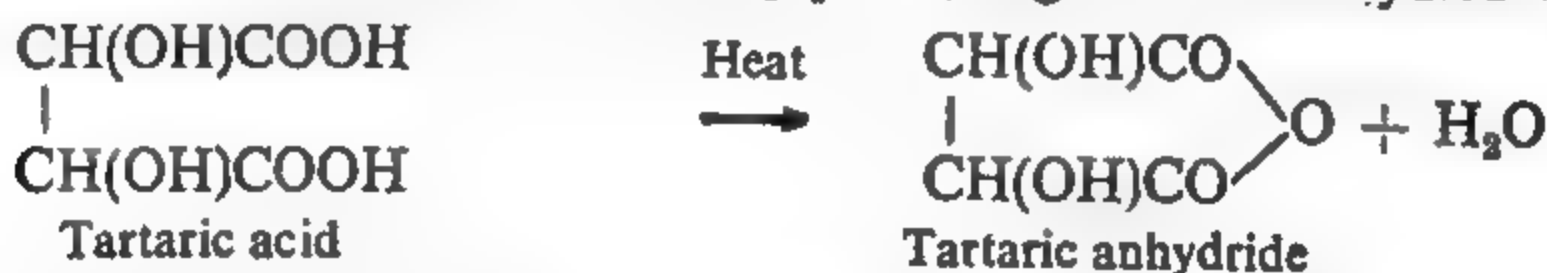
(2) On heating with hydrobromic acid, it gives dibromosuccinic acid.



(3) On warming with concentrated hydriodic acid, it is reduced to succinic acid.



(4) On heating above its melting point, it gives the anhydride.



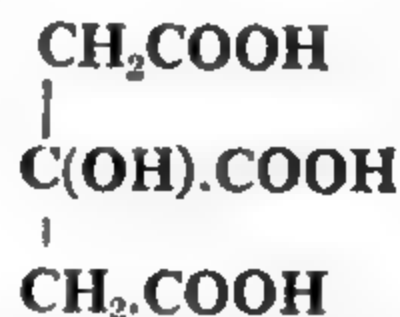
(5) On heating with concentrated sulphuric acid, it gets 'charred' with the simultaneous evolution of CO, CO₂ and SO₂.

Uses. Tartaric acid is used in the preparation of effervescent salines along with sodium bicarbonate. The salts of tartaric acid are used in medicine and industry, for instance, potassium acid tartrate is used for making baking powders; tartar emetic is used as a mordant in dyeing and in medicine and Rochelle salt is used in silvering of mirrors.

Test. Tartaric acid can be identified by the following tests:

1. On heating in a dry test tube, tartaric acid gets charred giving a smell of burnt sugar.
2. On heating with concentrated sulphuric acid, charring takes place with the evolution of CO, CO₂ and SO₂, accompanied by a smell of burnt sugar.
3. On warming the acid with a few drops of resorcinol solution, a violet red coloration is obtained.
4. On adding silver nitrate solution to a neutral solution of tartaric acid, a white precipitate is obtained. The precipitate dissolves in ammonia and on warming, a silver mirror is obtained.

CITRIC ACID, (2-Hydroxy 1,2,3, tricarboxy-propane)



Citric acid occurs widely in the free state in vegetable kingdom. The juice of all fruits with sour taste, such as lemons, *galgals*, unripe oranges etc., contains citric acid.

Preparation. Citric acid is obtained from two sources:

- (1) From lemons. Large quantities of citric acid are prepared from the juice of lemons which contains about 5–10 per cent of citric acid. The juice is first boiled to coagulate the albuminous matter which is removed by filtration. The filtered juice is then neutralised by chalk (CaCO₃) and boiled when citric acid gets precipitated as calcium citrate. The latter is separated by filtration and decomposed by a calculated

amount of sulphuric acid. The calcium sulphate formed, being insoluble, is removed by filtration and the filtrate containing citric acid is evaporated to get crystals of citric acid.

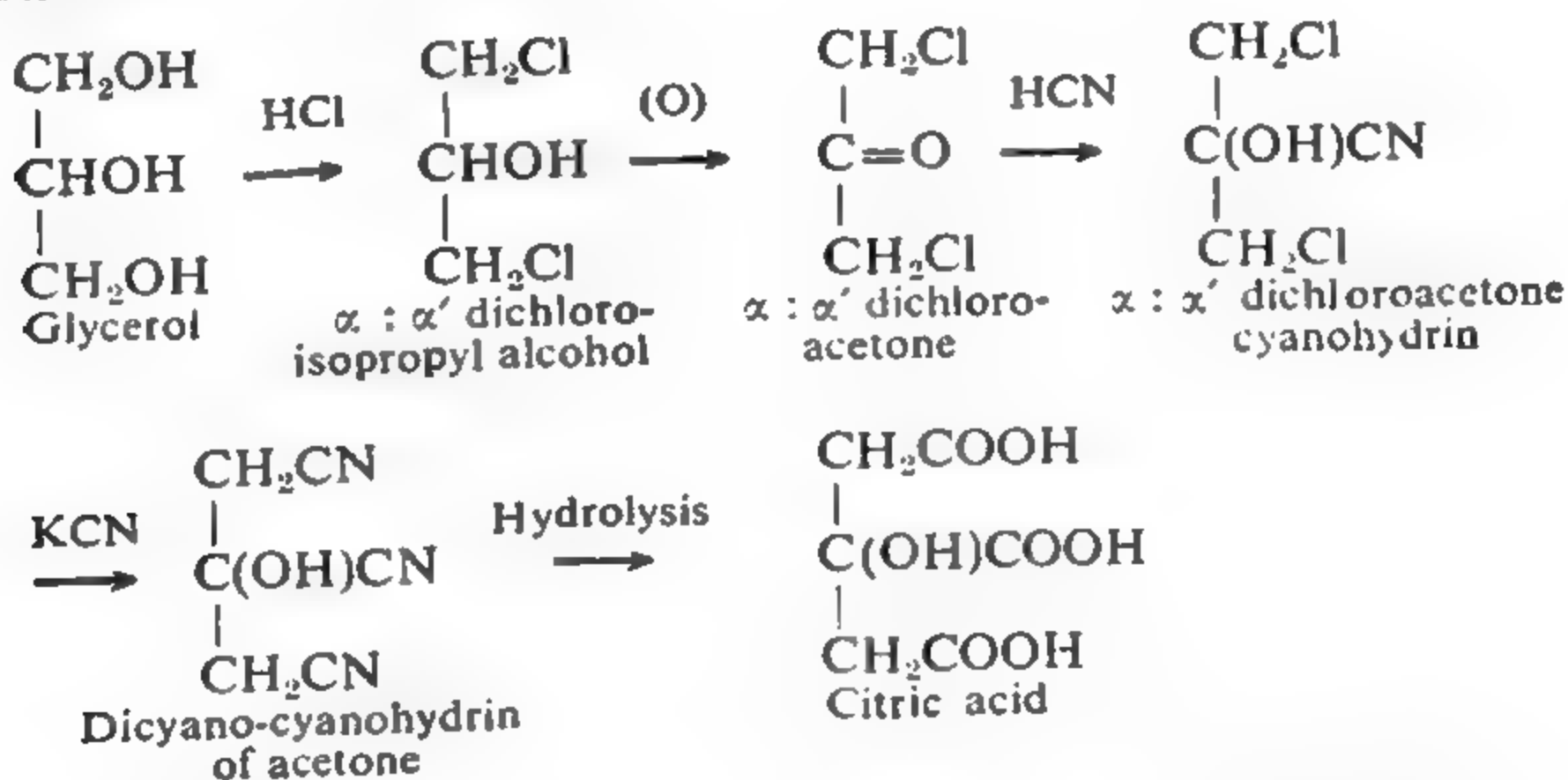
(2) From sugars (molasses). Till 1922, about 90 per cent of the world supply of citric acid was produced from lemon juice. But recently, a more economical method has been developed for the preparation of citric acid. It involves the fermentation of a dilute solution of molasses in the presence of certain inorganic salts by a special mould, *aspergillus wentii*, in acidic solution (pH 1 to 2). The mechanism of the reaction is not clearly understood.

In the U.S.A., England, Japan and some other countries, citric acid is now chiefly manufactured by the fermentation process.

Synthesis. Citric acid can be synthesised from its elements, as shown below :

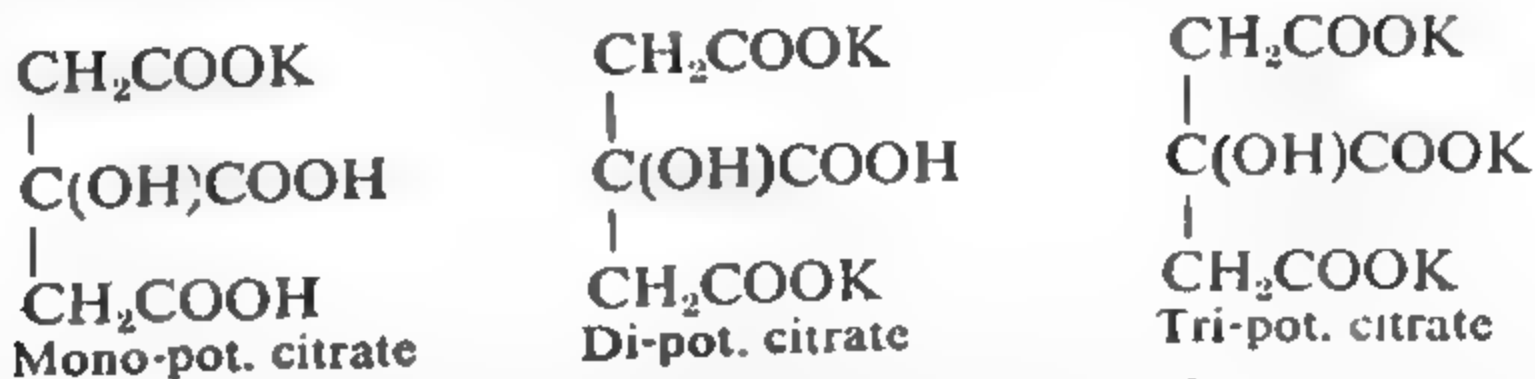
First step is the synthesis of glycerol (see chapter XXXI).

Further :



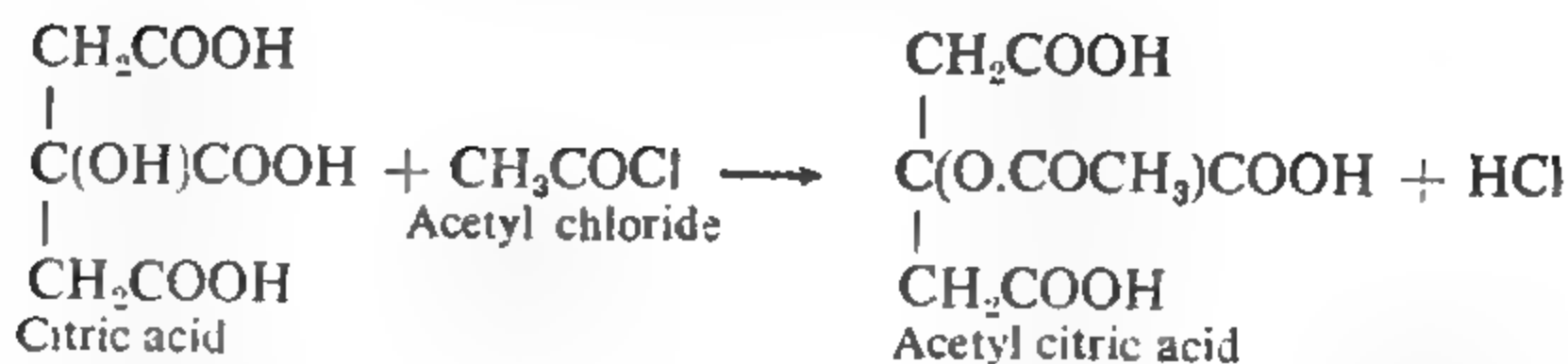
Physical Properties. Citric acid crystallises in the form of large prismatic crystals with one molecule of water of crystallisation. It is readily soluble in water and alcohol but is sparingly soluble in ether.

Chemical Properties. (1) Being a tribasic acid it forms three series of salts with alkalies. For example,

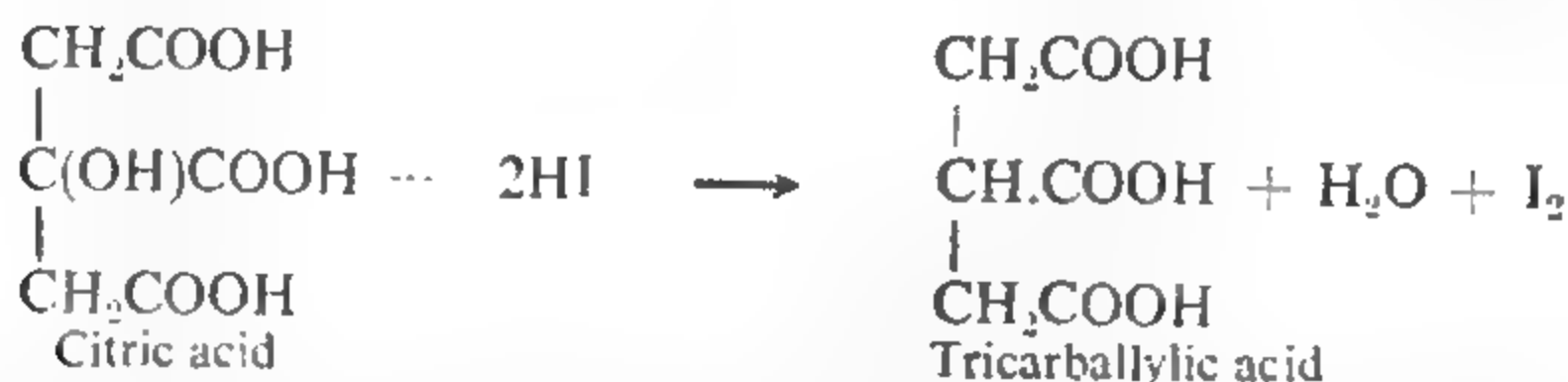


Similarly, with alcohols, say ethyl alcohol, it forms mono, di and triethyl citrates.

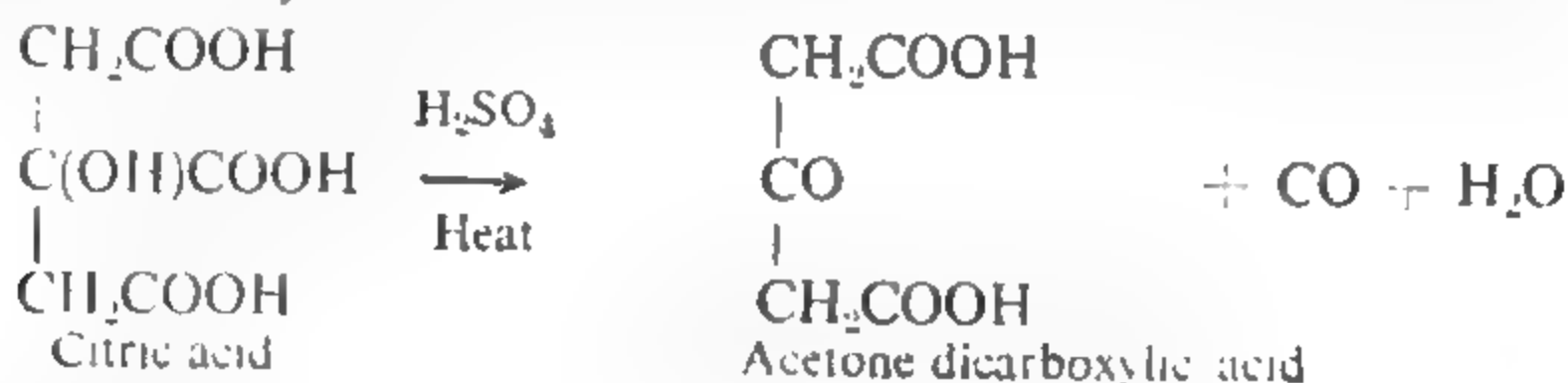
(2) On treatment with acetyl chloride, it gives *monoacetyl derivative*, showing the presence of one hydroxyl group.



(3) On heating with hydriodic acid, it is reduced to *tricarballic acid*.



(4) On heating with concentrated sulphuric acid, it decomposes to give *acetone dicarboxylic acid*.



(5) On heating to 150° , it loses a molecule of water giving an *unsaturated acid*.



Uses. Citric acid is used as a mordant in dyeing and calico printing. It is used in the preparation of effervescent saline along with sodium bicarbonate. Its salts are used in medicine, and for making blue prints.

OPTICAL ACTIVITY, POLARISATION OF LIGHT

If ordinary light is made to pass through a Nicol prism, it gets *polarized*, that is, the aether vibrations in the emergent ray take place in a single plane. The Nicol prism is called the *Polarizer*. Now if a second Nicol prism is placed in the path of the emergent beam with its axis perpendicular to that of the first (polarizer), the light remains visible but if it is placed at an angle to that of the first, no light will get through and the field of view will be dark. If a glass cell containing water is placed between the two Nicol prisms (with their axes at right angles to each other), the field of vision still remains dark but if, instead of water, some transparent solution of cane-sugar is placed in the cell, the field is brightened up and the second prism will have to be rotated through a certain angle for 'extinction' of the light. This shows that the plane of polarized light has been rotated through a certain angle. The

substances which cause rotation of the plane of polarized light are said to be **optically active**.

The rotation may be to the right or to the left. An optically active substance is called **dextro-rotatory**, if it causes rotation to the right and **laevo-rotatory**, if it causes rotation to the left.

The angle of rotation depends on the nature of the substance, the length of the column through which the light passes, the density of the liquid (or the concentration, if the substance is contained in a solution), the temperature and the wave-length of the incident light.

Thus, rotation R , may be given by the equation :

$$R = [\alpha]_{\lambda}^t \cdot l \cdot \frac{m}{v}$$

where l is the length of the column in decimeters through which the light passes, m is the weight of the optically active substance in grams occupying volume v c.c. and

$[\alpha]_{\lambda}^t$ is a constant which depends upon the nature of the substance, temperature (t) and wavelength (λ) of the light used and is called the **specific rotation** of the substance. It is a characteristic constant of a substance under given conditions of temperature and wave-length of light used. Since sodium light is generally used in such cases, the specific rotation may be expressed as :

$$[\alpha]_D^t = \frac{R \cdot v}{l \cdot m}$$

Thus, the specific rotation may be defined as the angle of rotation of the plane of polarized light produced by a liquid which in a volume of 1 c.c. contains 1 gram of the active substance, when the length of the column through which the light passes is 1 decimeter.

If the active substance is used as such, then $\frac{v}{m} = \frac{1}{d}$ and

$$[\alpha]_D^t = \frac{R}{l \cdot d}$$

where d is the density of the substance.

If the substance is in solution, the concentration must be taken into account and the expression may be put as

$$[\alpha]_D^t = \frac{100R}{l \cdot c}$$

where c is the number of grams of this substance in 100 ml. of the solution.

Measurement of Rotatory Power. The instrument used for measuring the angle of rotation of the plane of polarized light is known as **Polarimeter**. It consists essentially of two Nicol prisms mounted on the axis of the instrument. The first prism called **polarizer** is fixed and the other called **analyser** can be rotated about the axis of the instrument. A tube containing an optically active liquid (or a solution of an optically active substance) is placed in the path of the light between the two Nicols. The length of the tube is definite, varying from 5 cm. to 25 cm. (See Fig. 1. for a diagrammatic sketch).

A beam of monochromatic light (usually sodium light) is passed through the instrument without the tube containing the liquid. The light gets polarized by the first Nicol and then falls on the second which is rotated gradually so as to cut out the light completely. The reading on the scale is taken at this stage. It corresponds to zero reading.

The tube containing the liquid is then inserted. On looking through the

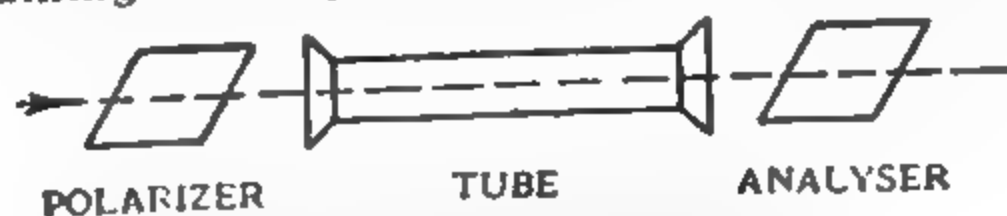
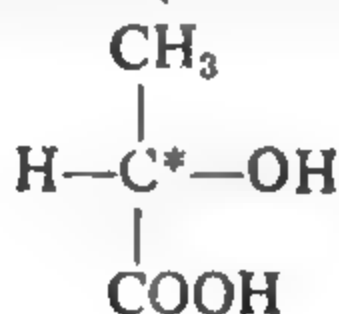


Fig. 1. Principle of Polarimeter.

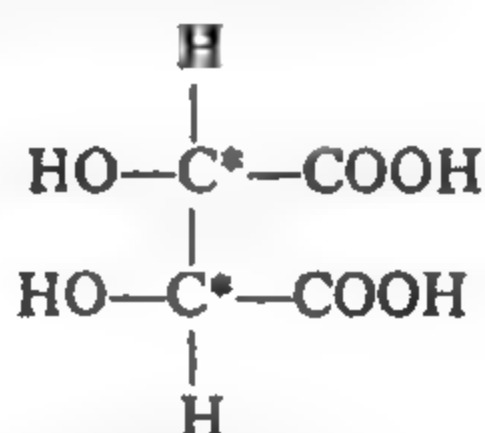
polarimeter, the field will appear bright since the optically active substance has rotated the plane of polarized light through a certain angle. The analyser is turned towards the right or left as may be required so as to get complete darkness again. The reading of the scale is taken. The difference between this and the first reading gives the required angle of rotation.

Optical Activity and Chemical Constitution.

It is found, in general, that optically active organic compounds consist of molecules which have at least one *asymmetric carbon atom*; that is, a carbon atom to which four different atoms (or groups) are attached. Lactic acid, for instance, contains one and tartaric acid contains two such carbon atoms (marked with asterisks) as shown below :



Lactic acid



Tartaric acid

Van't Hoff and Le Bel explained the connection between optical activity and molecular asymmetry and laid the foundation of the science of stereochemistry. According to them the four valencies of a carbon atom are directed in different planes towards the four corners of a regular tetrahedron, the carbon atom itself lying at the centre as shown in Fig. 2.



Fig. 2. Tetrahedral structure of carbon atom.

When the four groups are *all different*, as in lactic acid, it can be shown by models that there are two ways of arranging the groups about the central carbon atom as represented in Fig. 3.

The two molecules, obviously, are exact mirror images of each other and cannot be *superposed* upon each other. If one form is the dextro-rotatory, the other should be laevo-rotatory.

An equimolecular mixture of the two is known as the **racemic form**. This is optically inactive but can be resolved into the two active forms.

The dextro, laevo and racemic forms differ only in optical activity. They are almost identical in all other respects.

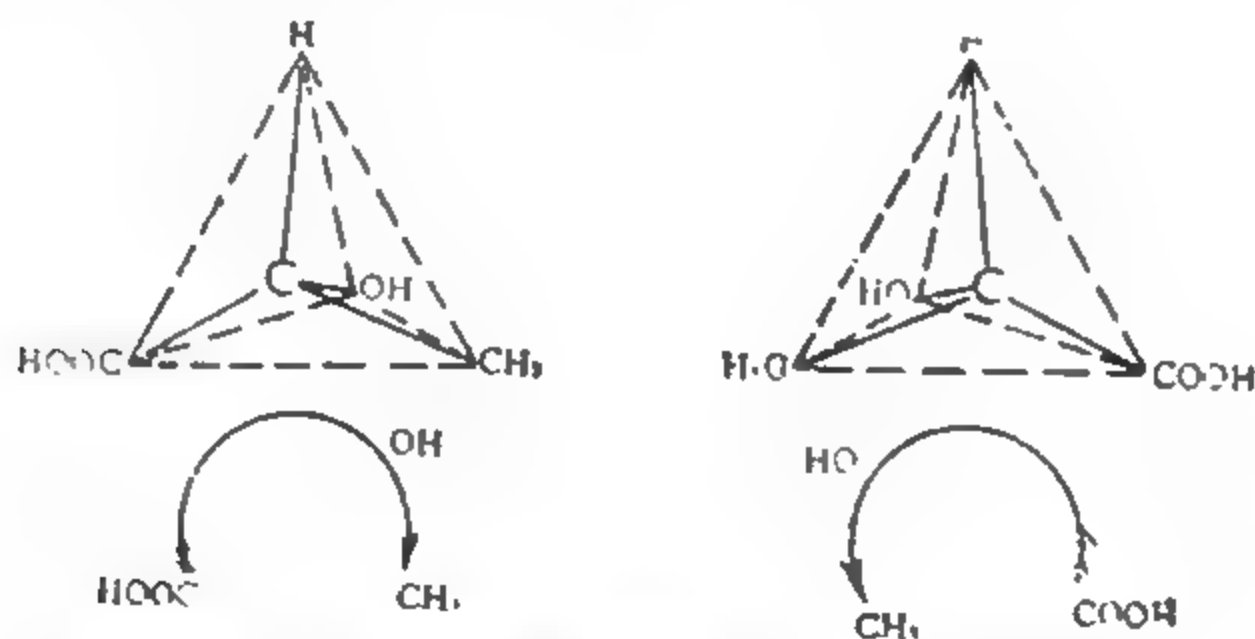


Fig. 3. Spatial configurations of lactic acids.

SUBSTITUTED CARBOXYLIC ACIDS

It may be mentioned that optical activity is also exhibited by compounds containing asymmetric atoms of nitrogen, silicon, tin, etc.

QUESTIONS

1. How is chloro-acetic acid prepared? Describe its important properties and uses.
2. Give the methods for the preparation of glycine. Describe its important properties and uses.
3. How is amino acetic acid prepared? Show that it behaves both as an acid and as an amine. What is a 'zwitterion'?
4. Describe the various methods for the preparation of glycollic acid. Show that it behaves both as an acid and a primary alcohol.
5. How can lactic acid be prepared? Describe its important properties and uses.
6. Give in detail the methods for the technical production of lactic acid. How can the acid be synthesised from carbon and hydrogen?
7. Describe the methods for preparing tartaric acid on a commercial scale. What happens when tartaric acid is heated with (i) HI (ii) Sulphuric acid? Mention its important uses.
8. How is citric acid obtained from (i) Lemons (ii) Sugars? Give the complete synthesis of the acid and show what happens when citric acid is heated with HI and with sulphuric acid.
9. Give the complete syntheses of the following :
(i) Lactic acid (ii) Tartaric acid (iii) Citric acid (iv) Glycollic acid and (v) Glycine.
10. What is meant by optical activity and optical isomerism? Discuss the optical isomerism of lactic acid? (Panjab Inter 1961)
11. (a) How is tartaric acid synthesised from elements? (Panjab Inter 1960 S)
(b) Write equation and name of the product when tartaric acid is reduced with HI.
(c) Explain, with one example, what is meant by optical isomerism. (Panjab Inter 1960)
12. Write illustrative but brief note on optical or stereoisomerism. (Panjab Inter 1959 S)
13. Show how lactic acid may be produced from propionic acid and from acetaldehyde; how will you name it as a derivative of the former? (Panjab Inter 1956)
14. Give the preparation of citric acid. How does it react with (i) hydrogen iodide and (ii) hot conc. sulphuric acid? (Panjab Inter 1953)
- How can the acid be synthesised from its elements? (Panjab Inter 1952)
15. What are amino acids? How are they related to proteins? What is their importance? Give the preparation and properties of amino acetic acid. (Panjab Inter 1952)
16. Describe briefly the preparation of lactic acid from glucose. Give five properties of the acid and explain why it cannot be purified by distillation at ordinary pressure. (Panjab Inter 1959 S)
17. Describe the laboratory preparation of amino-acetic acid. When is the action of (a) heat (b) caustic soda (c) hydrochloric acid (d) nitrous acid and (e) acetyl chloride on the acid? (Panjab Inter 1950)
18. Write a short note on optical activity. (Panjab Inter 1952)

CHAPTER XXXIX

OILS, FATS AND SOAPS

Oils and Fats. Oils and fats are the *triesters of glycerol* with various long chain organic acids, both saturated and unsaturated. These triesters are usually known as **glycerides**.

Oils are liquids at ordinary temperatures while fats are solids. The glycerides constituting **oils** contain a larger proportion of **unsaturated acids**, such as oleic acid, $C_{17}H_{33}COOH$; linoleic acid $C_{17}H_{31}COOH$, etc., while the glycerides forming the **fats** contain a larger proportion of **saturated acids** such as lauric acid, $C_{11}H_{23}COOH$; myristic acid, $C_{13}H_{27}COOH$; palmitic acid, $C_{15}H_{31}COOH$ and stearic acid, $C_{17}H_{35}COOH$.

The glycerides are named according to the acid radical present in them. For instance, the glyceride containing stearic acid radical is called *stearin* or *tristearin* and the one containing the palmitic acid radical is named as *palmitin* or, *tripalmitin*.



Stearin or tristearin



Palmitin or tripalmitin

Usually more than one acid radical is present in the same glyceride. These are called mixed glycerides. The naturally occurring oils and fats are generally mixtures of such 'mixed glycerides'. For instance,



Oleo-palmito-stearin



Palmito-distearin



Stearo-dipalmitin

Occurrence and Extraction. Oils and fats are widely distributed in nature in plant and animal kingdom. In plants, they are found chiefly in seeds while in animals, they are present under the skin and in muscles.

From animals, the fat is obtained by the process known as **rendering**. In this process, the animal tissues containing the fat are chopped off and then heated with water or steam. The fat melts and forms a separate layer at the top from where it is removed from time to time.

From seeds, the oils are obtained in the following steps :

(1) *Cold compressing.* The seeds are crushed by rollers and then pressed in hydraulic presses in the cold. This gives the best grade oil.

(2) *Hot pressing.* The pressed cake, obtained above, is then heated and pressed further. This gives second grade oil.

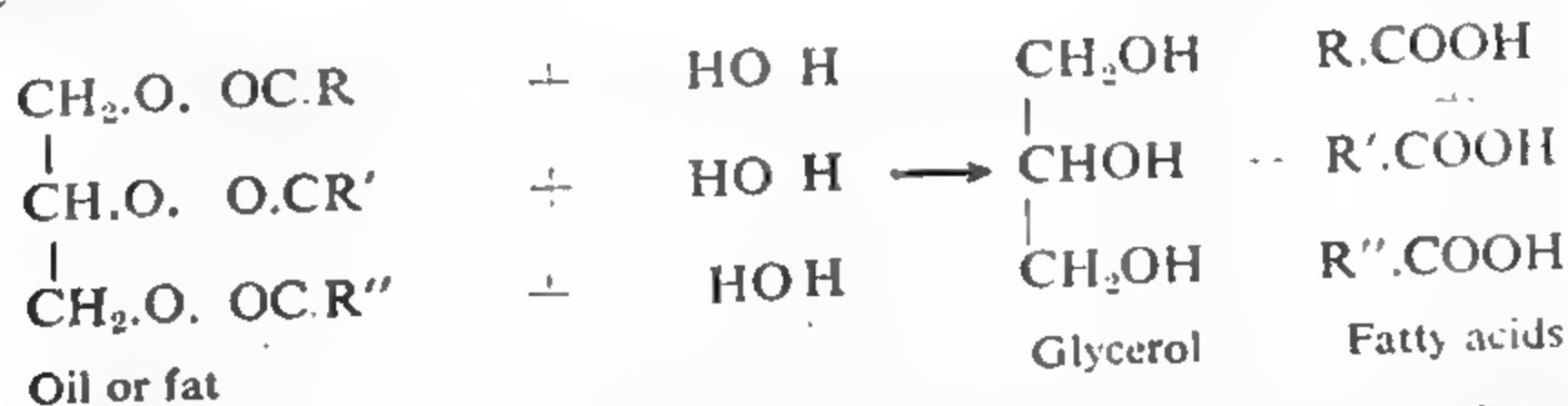
(3) *Extraction by solvent.* The pressed cake, after hot pressing, is crushed and extracted with organic solvents, such as petroleum ether, benzene, carbon tetrachloride, to obtain a further quantity of the oil.

Refining. The crude oil or fat obtained above is treated with a little alkali to neutralise the free acids. The alkali also coagulates any colloidal impurities present. The oil is then bleached by warming with animal charcoal or plaster of Paris or Fuller's earth and deodorised by treatment with steam.

Physical Properties. Oils and fats are liquids or solids (depending upon prevailing temperatures) having no smell or taste, if pure. They are lighter than and immiscible in water. They are freely soluble in organic solvents such as petroleum ether, benzene, chloroform, etc. The fats containing a larger proportion of high melting *saturated* acids, such as stearic acid (m.p. 68°), palmitic acid (m.p. 63°), melt at high temperatures while the oils, containing a greater proportion of low melting *unsaturated* acids, such as oleic acid (m.p. 14°), melt at lower temperatures.

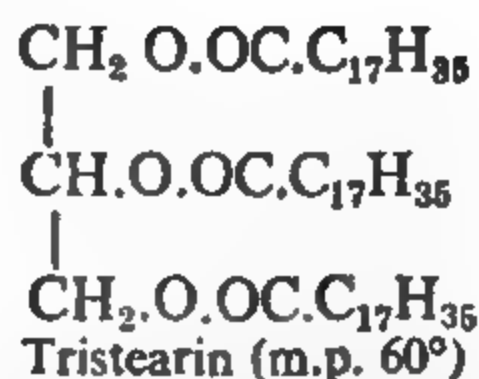
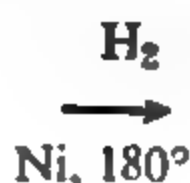
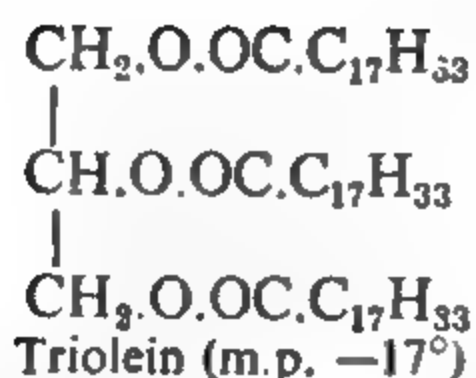
Chemical Properties. Oils and fats are typical **natural esters** and give the usual reactions of this class of compounds. Besides, the unsaturated acids (e.g., oleic acid) present in oils contain ethylenic linkages and hence the oils also give addition and oxidation reactions. Two important reactions of oils and fats are (i) *Hydrolysis* and (ii) *Hydrogenation*.

(1) **Hydrolysis.** Oils and fats are easily hydrolysed on heating with water alone or in the presence of mineral acids to yield glycerol and free organic acids.



When hydrolysed by alkalies, the resulting products are glycerol and sodium salts of fatty acids (*viz.*, *soaps*), and the process is termed **saponification**.

(2) **Hydrogenation.** The *liquid* glycerides containing unsaturated acids (oleic acid, linoleic acid, etc.) add on hydrogen in the presence of finely divided nickel giving *solid* glycerides. The unsaturated oleic acid radical changes into the saturated stearic acid radical as a result of which the melting point of the liquid glyceride rises and hence it hardens to become a solid. For example,



This process of converting liquid glycerides (generally oils) into solid ones (fats) by hydrogen is known as **hydrogenation** or **hardening of oils**. Vegetable ghee is prepared from linseed oils and ground-nut oil by this process.

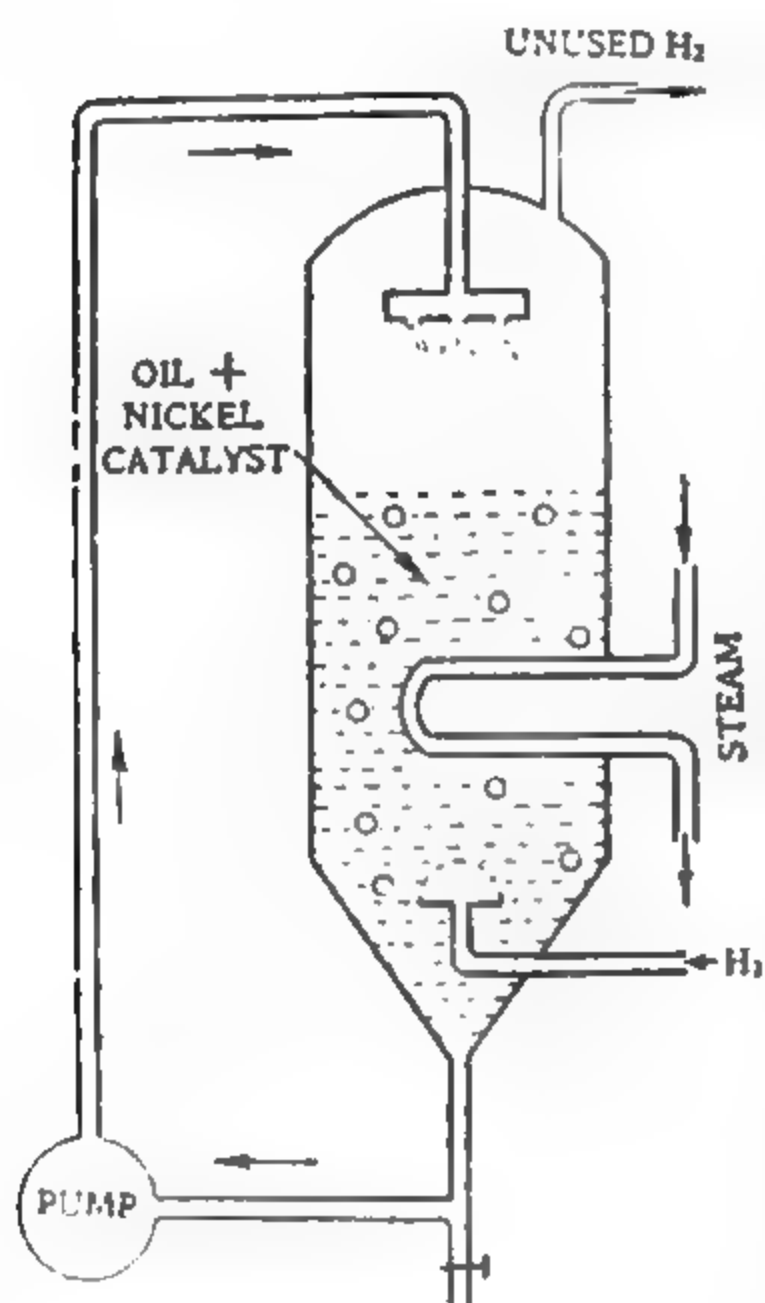


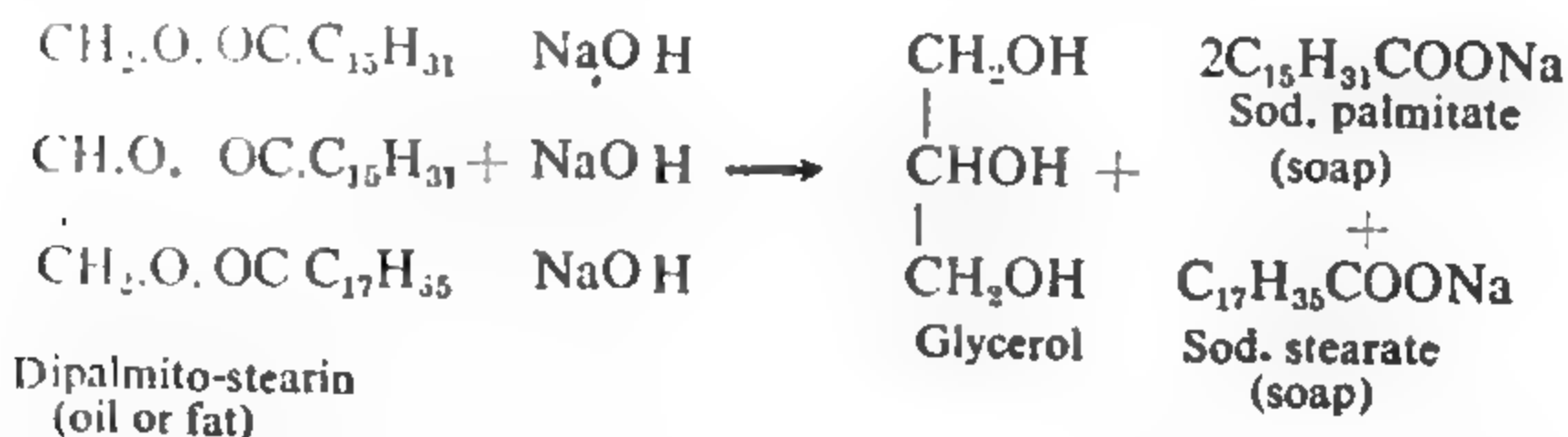
Fig. 1. Hydrogenation of oils.

A simple type of hydrogenator is shown in Fig. 1. It consists of a vertical iron tank provided with closed steam coils for heating purposes. The oil is taken in the tank and mixed with a suitable amount of the nickel catalyst. It is then heated by passing steam through the steam coil and hydrogen gas is admitted from below. The unused hydrogen escaping at the top is collected and used again. The oil is kept in circulation with the help of a pump as shown.

The reaction is exothermic and as a result the temperature rises automatically. The conditions are so adjusted that the temperature is maintained at the optimum level of 180° . Hydrogenation is continued till the desired consistency is reached. The molten fat is then taken out and filtered in the filter press to eliminate the nickel catalyst. The resulting product is a colourless solid resembling ghee and is usually known as '**vanaspati ghee**'.

SOAPS

Soaps are mixtures of sodium or potassium salts of higher fatty acids such as stearic acid, palmitic acid, oleic acid. They are usually obtained by the hydrolysis of oils and fats with sodium or potassium hydroxide. For example,



The sodium soaps are generally hard in consistency and are known as **hard soaps**. The potassium soaps, on the other hand, are comparatively soft and more soluble and are referred to as **soft soaps**. Shaving creams, vanishing creams, shampoos, etc., are all potassium soaps.

Manufacture of Soap. The following are the common processes for the manufacture of soap.

1. **The Cold Process.** In this process, the molten fat or oil is mixed with the required amount of *soda lye* (sodium hydroxide solution) in open pans and vigorously stirred by mechanical stirrers till the soap begins to set. At this stage, it is transferred to frames and allowed to solidify there. The solid soap is cut into bars or cakes, dried and put in the market as *washing soap*.

2. **The Hot Process.** As the name implies, this process consists in carrying out the hydrolysis of the oil or fat at high temperatures. A diagrammatic sketch of the plant is shown in Fig. 2.

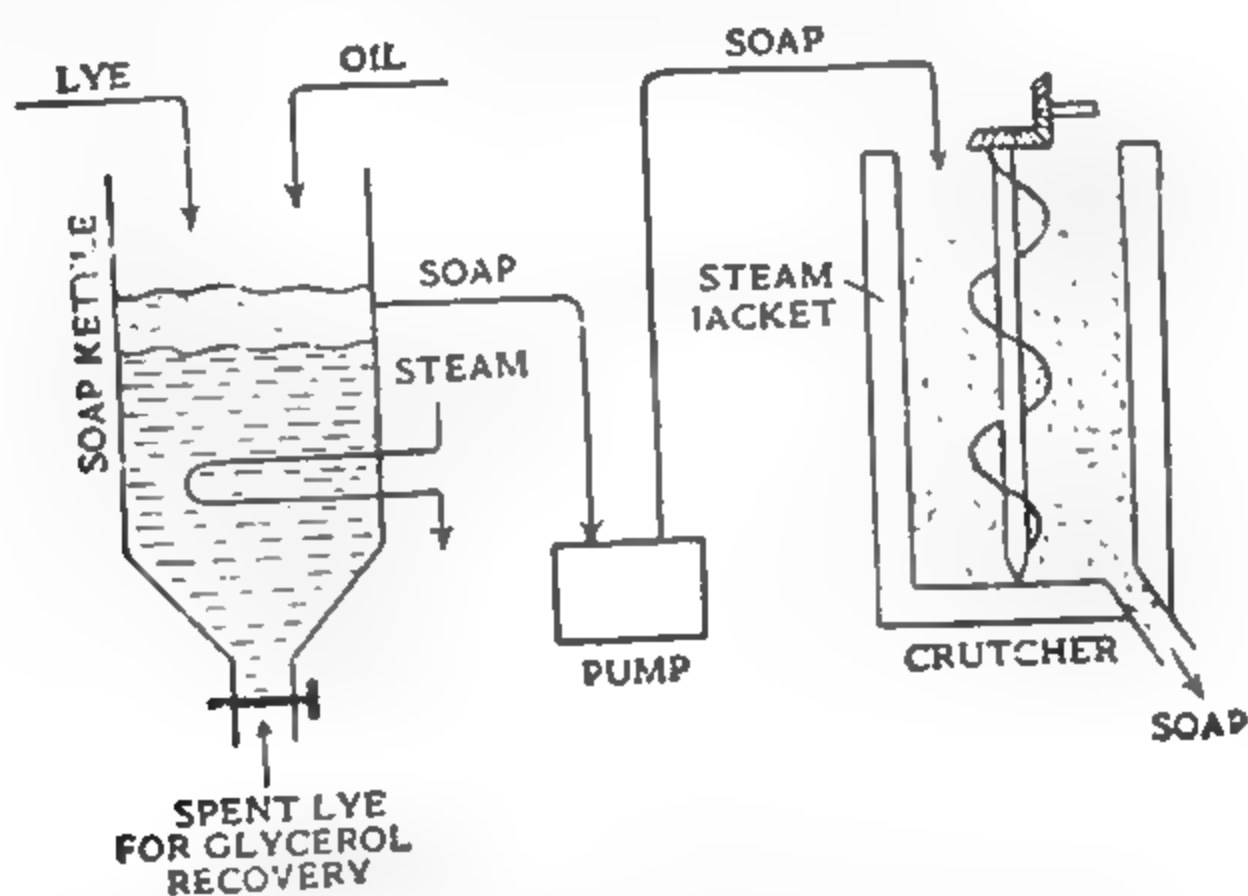


Fig. 2. Manufacture of soap by hot process

The oil or molten fat (*soap stock*) is taken in the *soap kettle* and excess of sodium hydroxide solution (*soda lye*) added to it. The mixture is boiled by passing steam through the open steam coils provided at the base of the kettle (not shown in the figure). This also keeps the contents in a state of good agitation throughout. During this treatment, about 80 per cent of the soap stock gets converted into soap.

The contents of the kettle are then heated by closed steam coils and excess of sodium chloride added to it. Due to the common ion effect, the soap is thrown out of the solution and rises to the top of the liquid in the form of a curdy mass. The lower aqueous layer (*spent lye*) containing glycerol is run off and treated for the recovery of glycerol. (see chapter XXXII).

The soap recovered from the solution is boiled with water to remove any alkali and the curdy mass rising to the top is transferred to the **crutcher** with the help of a pump as shown. Here it is mixed with a requisite dye and perfume and also with a *filling agent*, such as sodium silicate,

talc starch, borax, etc., and thoroughly stirred with the help of a mechanical stirrer. The crutcher is provided with a steam jacket in order to avoid the cooling and solidification of soap during crutching.

The soap is then drawn out in the frames and allowed to solidify. It is dried by hot air, milled and finally stamped into cakes.

The hot process is more economical than the cold process and yields a pure product because all impurities and excess of alkali are completely removed. Besides, glycerol, an important by-product, can also be recovered in this process.

3. **The Ittner's Continuous Process.** This has been developed recently and is getting very popular. In this process, a rapid hydrolysis of oils or fats is carried out by superheated water, under pressure, in the presence of a catalyst (lime or zinc oxide). Advantage is taken of the fact that superheated water and fat are appreciably miscible with each other. The oil or fat is fed into a vertical cylindrical vessel near the base and the water is admitted from the top. The water, being heavier, moves down while the oil or fat, being lighter, moves up. The water dissolves in the fat and reacts with it giving glycerol and free fatty acids. The latter, being lighter, rise to the top and are removed. The aqueous solution containing glycerol, being heavier, collects at the base. The fatty acids obtained are converted into soaps by interaction with a calculated amount of alkali. The aqueous solution (*sweet water*) is treated for the recovery of glycerol.

The hydrolysis of the fat is rapid and complete and the process is continuous.

QUESTIONS

1. What are oils and fats? What is the main difference between them? Describe briefly the occurrence, extraction and refining of oils and fats.

2. What do you understand by "Hardening of Oils"? Describe in detail a process for carrying out the hardening of oils.

3. What is meant by Hydrogenation of oils? Describe the preparation of vegetable ghee from groundnut oil.

4. What are soaps? Describe the hot process for the manufacture of soap.

5. What are oils, fats and soaps? Describe the modern continuous process for soap manufacture. What are the advantages of this process?

6. 'Ghee' is called a 'fat' and 'sarsen oil' an oil. Chemically, what are they? Give their names and formulae of at least four of the constituents that mainly combine together to produce 'fats' and oils. Hence, explain the difference, if any, between the two and explain how an oil can be converted into a fat. (Panjab Inter. 1954)

7. Distinguish between (i) mineral oils and vegetable oils (ii) oils and fats. What is "Vanispathi" or the so-called "Vegetable ghee"? How is it obtained commercially?

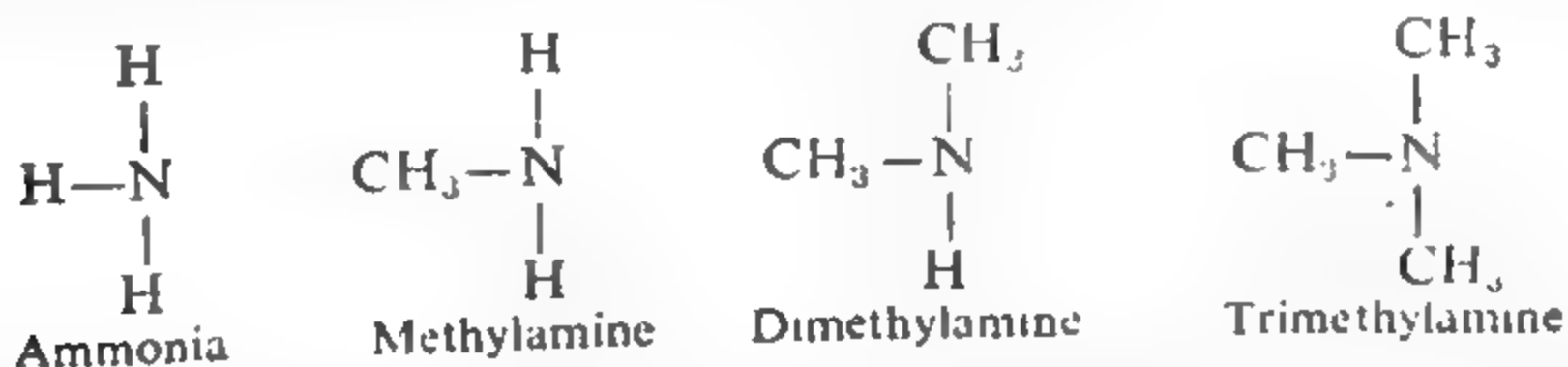
What is the action of alkalies on oils and fats? (Panjab Inter 1952)

8. What are oils and fats and how do they differ from mineral oils? What are their uses? Describe the process for the manufacture of soap and explain its cleansing action.

CHAPTER XL

THE ALIPHATIC AMINES

The amines can be regarded as derivatives of ammonia, in which one or more hydrogen atoms have been replaced by alkyl groups. Thus, CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$ are all derivatives of ammonia obtained by replacement of one, two or three hydrogen atoms by alkyl groups as shown by their structural relationship :



The amines are classified as *primary*, *secondary* or *tertiary* depending upon whether *one*, *two* or all the *three* hydrogen atoms of ammonia molecule are replaced by the same number of alkyl groups. In other words, the general formulae of primary, secondary and tertiary amines are RNH_2 , R_2NH and R_3N respectively.

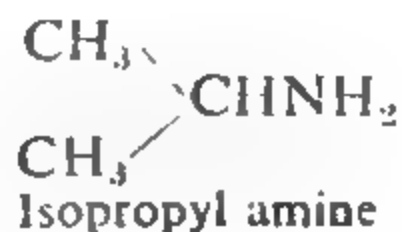
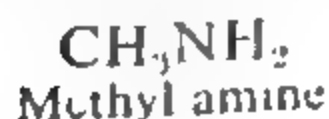
Besides amines, which are derivatives of ammonia, *quaternary ammonium compounds* (also known as *tetra-alkyl ammonium compounds*), in which all the four hydrogens of ammonium radical are replaced by alkyl groups, are also known. Thus, corresponding to ammonium hydroxide there is tetra-alkyl ammonium hydroxide.

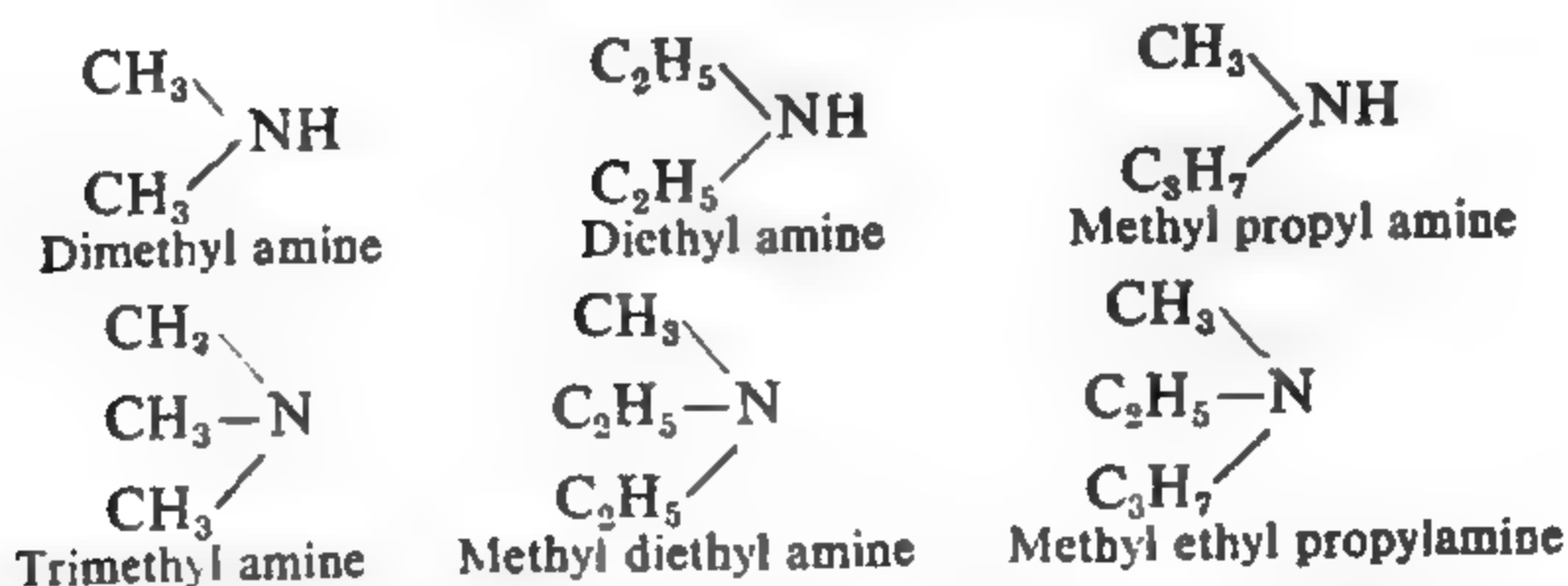


The amines are important organic bases.

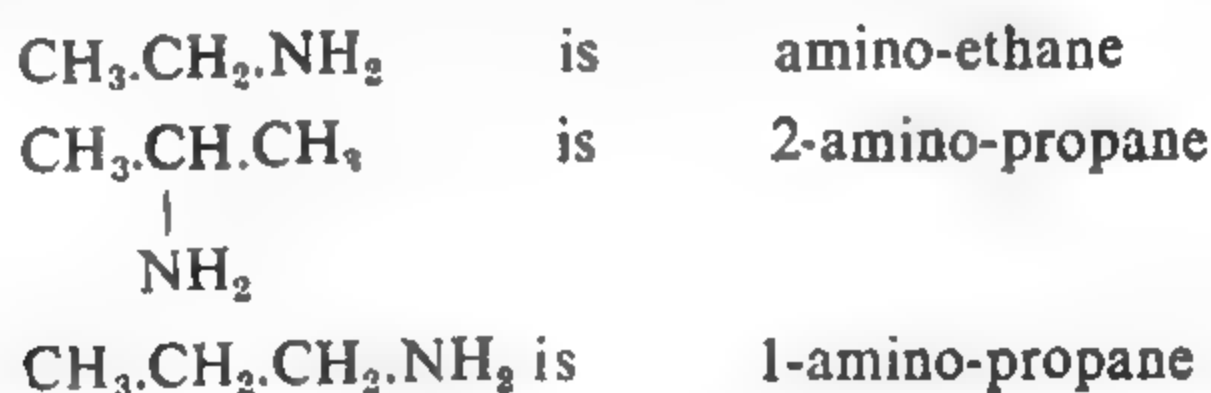
Nomenclature. Amines are named after the alkyl group or groups attached to the nitrogen atom, by adding the suffix 'amine' in each case.

For example,





The I.U.C. system looks upon amines as amino-derivatives of corresponding alkanes and are named after the parent hydrocarbon, the position of the amino group being indicated by a suitable number. Thus,

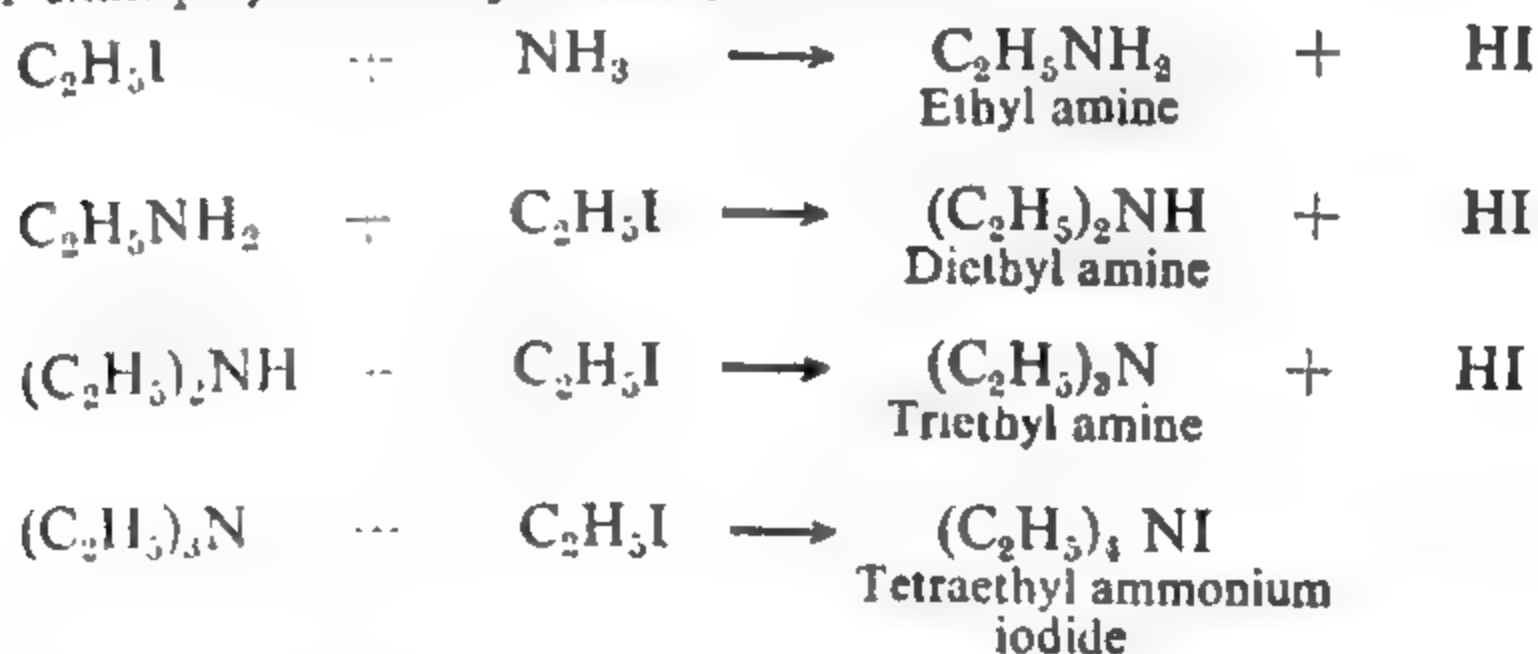


Methods of Preparation. The various methods for the preparation of amines can be studied under the following heads :

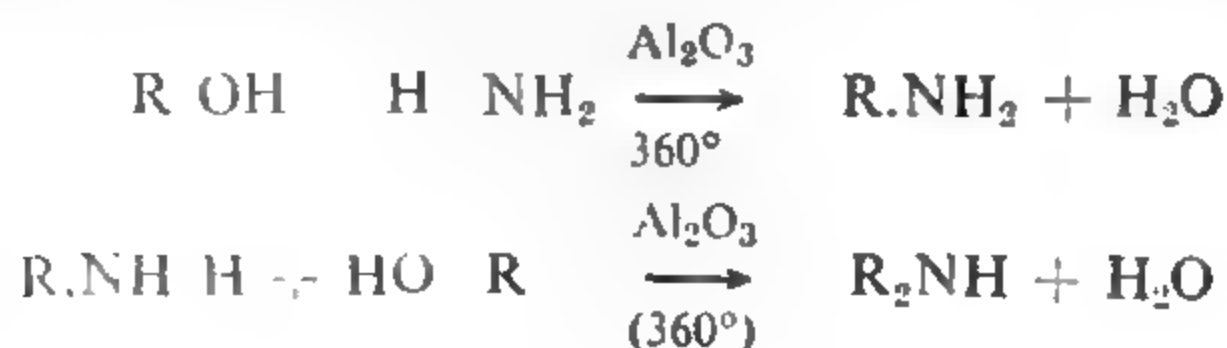
(a) **Methods yielding mixture of amines.**

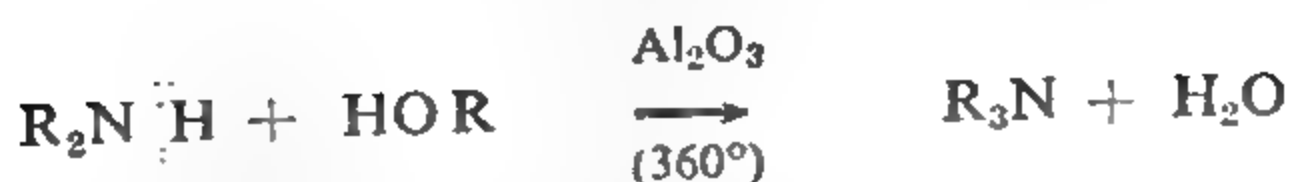
(1) **Hofmann's method (1850).** By heating an alkyl halide with an alcoholic solution of ammonia in a sealed tube at 100° , a mixture of all the three types of amines, along with some quaternary salt is obtained.

For example, with ethyl iodide, we have :



(2) **By ammonolysis of alcohols.** By passing a mixture of the vapour of alcohol and ammonia over heated alumina or thoria (360°), all the three types of amines are obtained.



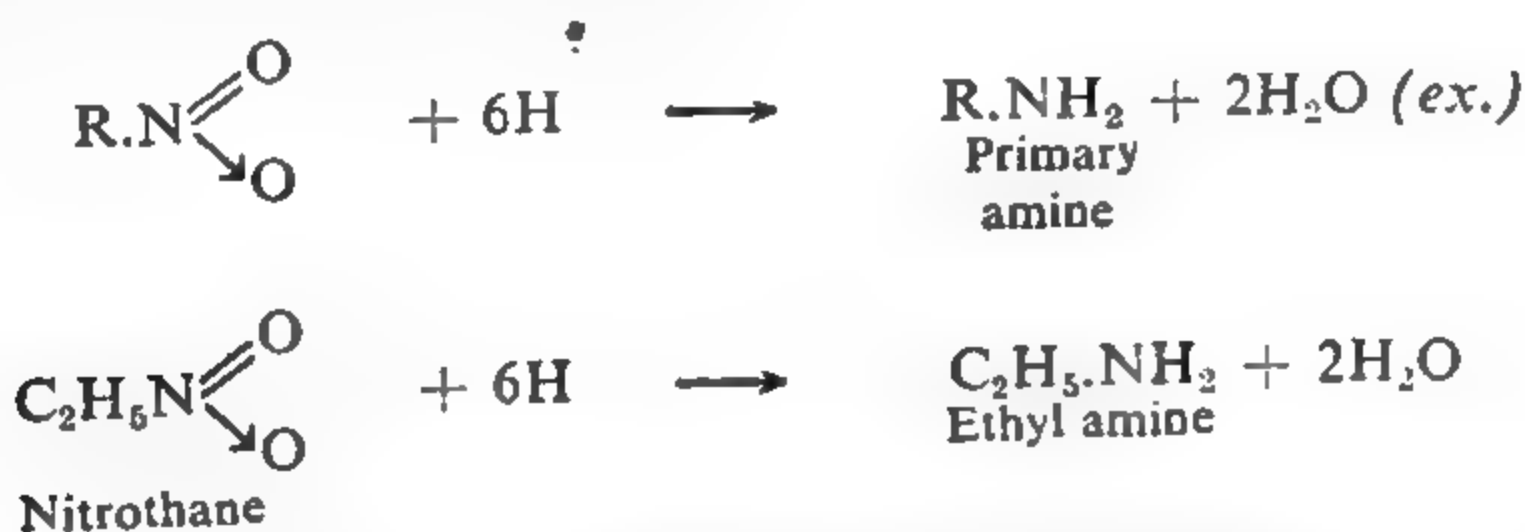


The mixture of amines obtained by either of the above methods can be separated, as described on page 493.

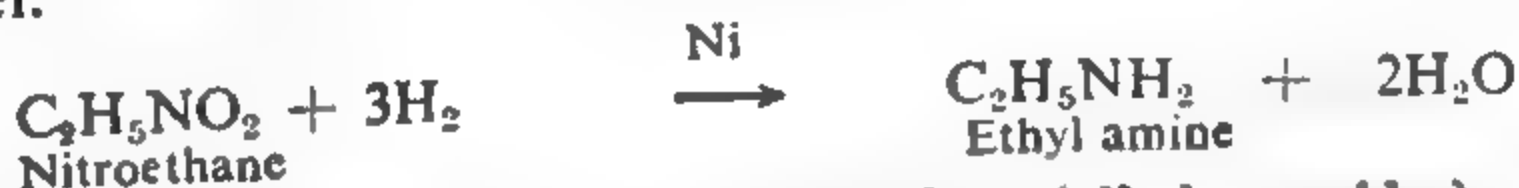
(b) Méthods yielding primary amines.

(1) By the reduction of nitro-paraffins. Nitro paraffins, when reduced with nascent hydrogen, yield primary amines.

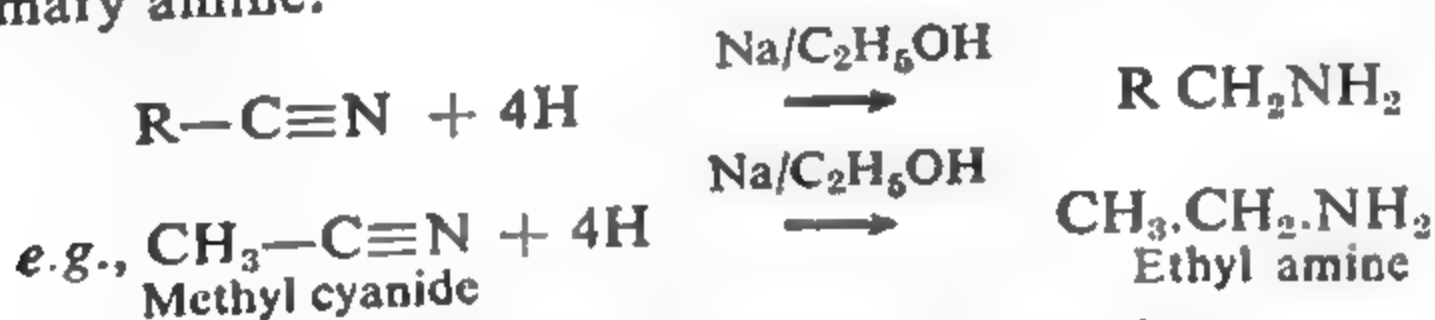
The nascent hydrogen is produced either by the action of sodium on alcohol or from tin and hydrochloric acid.



The reduction can also be carried out by hydrogen in the presence of nickel.

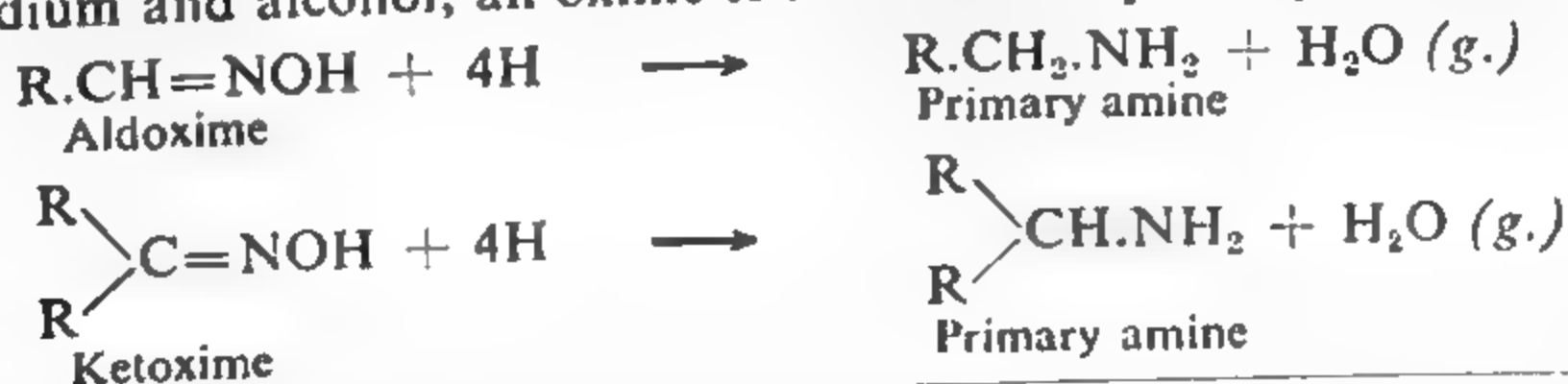


(2) By the reduction of acid nitriles (alkyl cyanides). Nascent hydrogen from sodium and alcohol reduces an alkyl cyanide to the primary amine.



This reaction, is called **Mendius reaction**.*

(3) By the reduction of oximes. With zinc dust and acetic acid or with sodium and alcohol, an oxime is reduced to a primary amine.



*Sabatier and Senderens have shown that when reduction of cyanides is carried out by hydrogen in the presence of finely divided nickel, the resulting product is a secondary amine and not a primary amine.



(4) **By the hydrolysis of alkyl isocyanates.** An alkyl isocyanate, on boiling with an alkali, yields a primary amine.



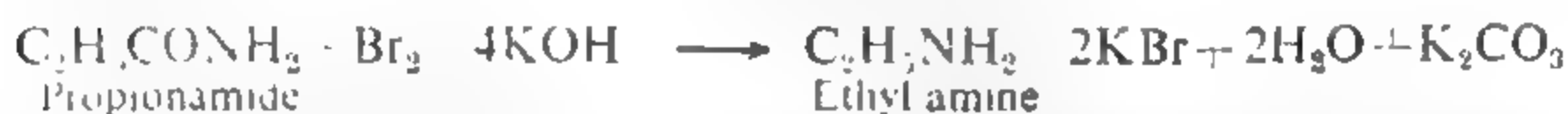
This method was first employed by Wurtz (1849).

(5) **By the hydrolysis of alkyl isocyanides.** On boiling with a dilute mineral acid, an alkyl isocyanide yields a primary amine and formic acid.



Ethyl isocyanide

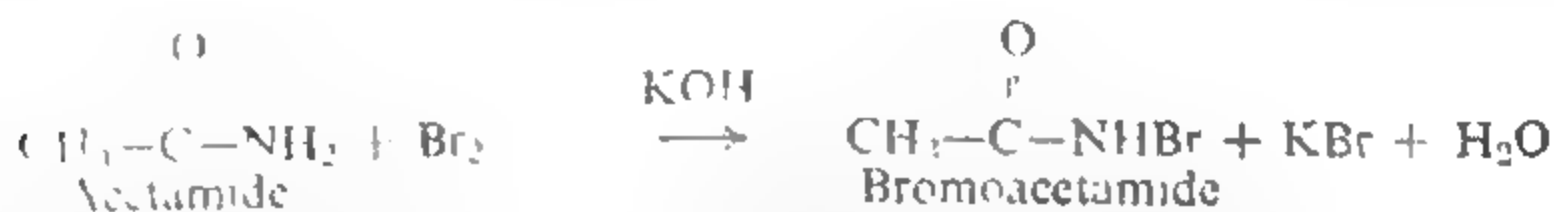
(6) **By treatment of the corresponding amide with bromine and alkali.** An acid amide, when treated with bromine and aqueous or alcoholic potash (or with sodium hypobromite or sodium hypochlorite), yields a primary amine.



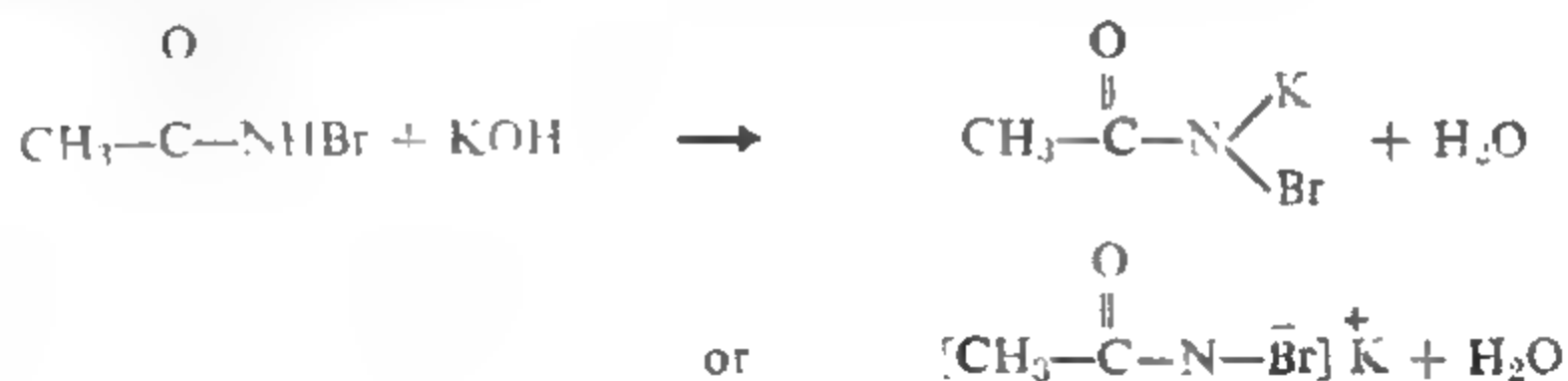
The above reaction is called **Hofmann's bromamide** or **hypobromite reaction** (1849) and is by far the most important method employed for the preparation of primary amines.

Mechanism of Hofmann's bromamide reaction. This reaction is supposed to take place in the following steps, taking conversion of acetamide into methylamine as an illustration.

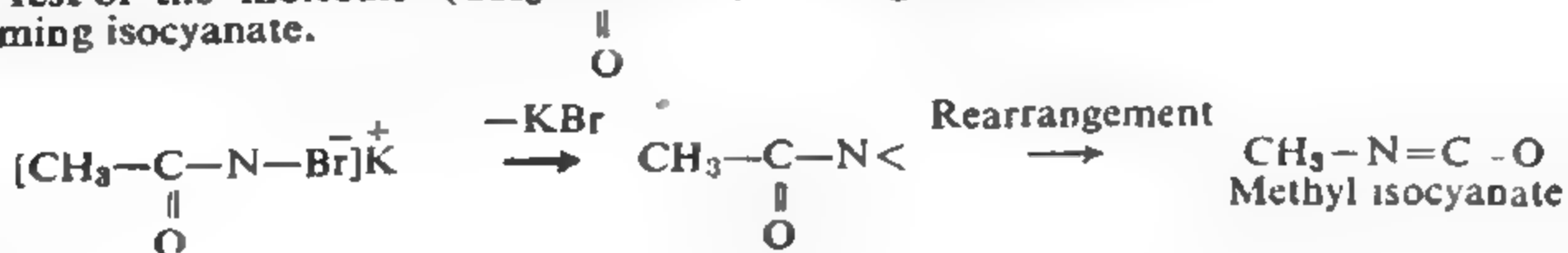
(i) The acid amide is first brominated.



(ii) The bromoacetamide then reacts with potassium hydroxide to form a potassium salt, which is ionic.



(iii) The potassium salt of aceto-bromamide is unstable, loses KBr molecule and the rest of the molecule ($\text{CH}_3-\text{C}-\text{N}<$) undergoes intramolecular rearrangement forming isocyanate.



(iv) The methyl isocyanate gets hydrolysed with alkali to give the primary amine.

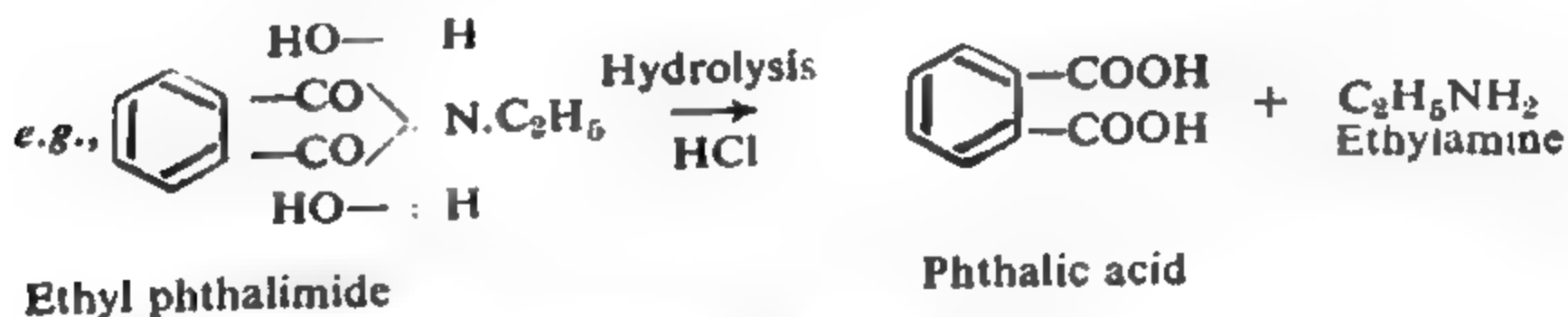
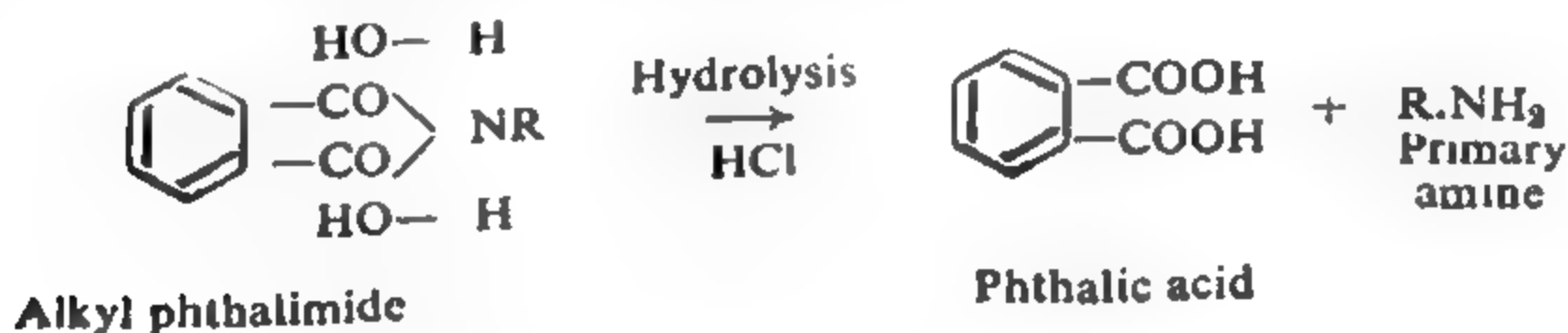


Hence, the overall equation is :



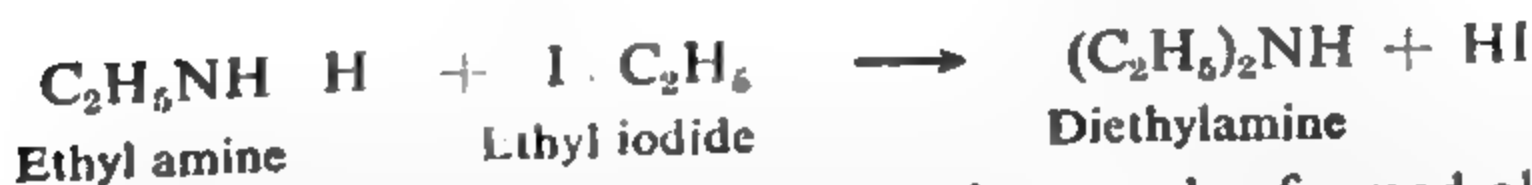
It is evident that the amine obtained contains one carbon atom less than the amide, hence this reaction is made use of in *descending a homologous series*.

7. By the hydrolysis of alkyl phthalimide with mineral acids (Gabriel's phthalimide reaction). In this method phthalimide is treated with alcoholic potash to yield potassium phthalimide which with an alkyl halide gives N-alkyl derivative. This N-alkyl-phthalimide on boiling with a dilute mineral acid yields a primary amine.



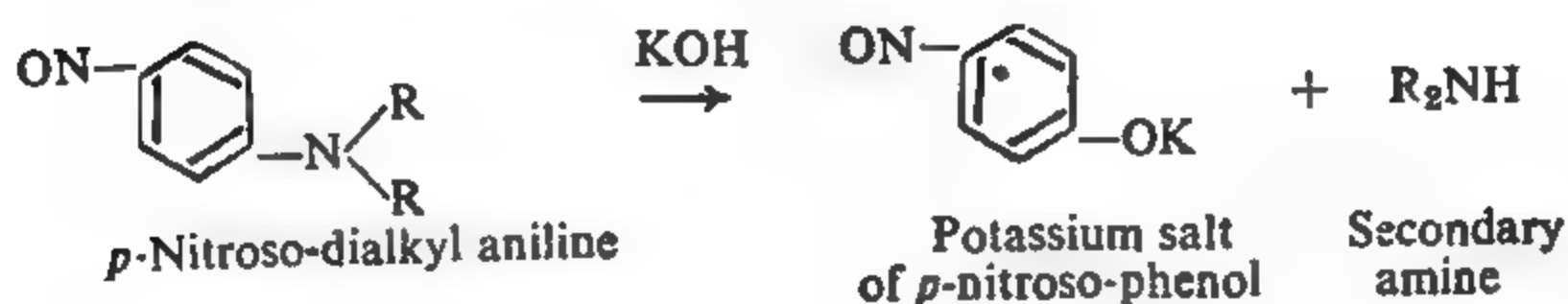
(c) Methods yielding secondary amines.

(1) By heating an alcoholic solution of primary amine with a calculated quantity of alkyl halide.

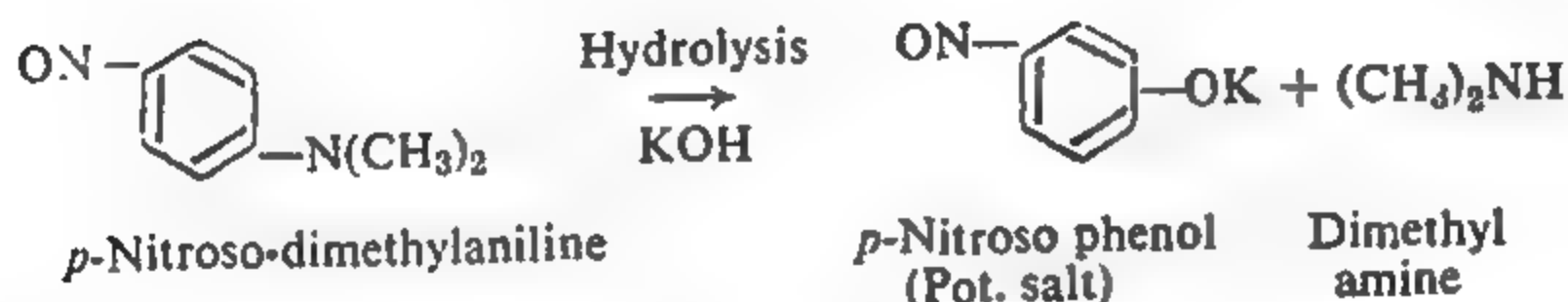


Tertiary amine and quaternary salts are also formed alongwith.

(2) By the hydrolysis of *p*-nitroso-dialkyl-aniline with strong alkali.



For example,



(3) By the reduction of alkyl isocyanide (or isonitrile) with nascent hydrogen. The method yields a secondary amine in which one of the alkyl groups is a methyl group.

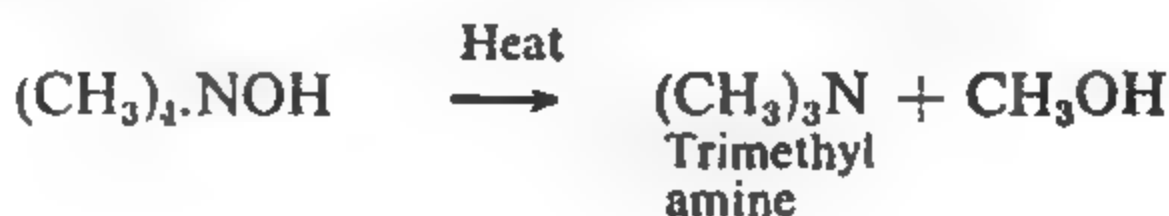


For example,



(d) Methods yielding tertiary amines.

(1) By the hydrolysis of the corresponding quaternary ammonium halide with moist silver oxide, followed by strong heating. A quaternary ammonium iodide when treated with moist silver oxide forms a tetra-alkyl ammonium hydroxide (quaternary ammonium hydroxide) which on heating decomposes to yield a tertiary amine and an alcohol.



(2) By treating a primary or a secondary amine with a calculated quantity of alkyl halide.



For obvious reasons, this method seldom yields a pure product.

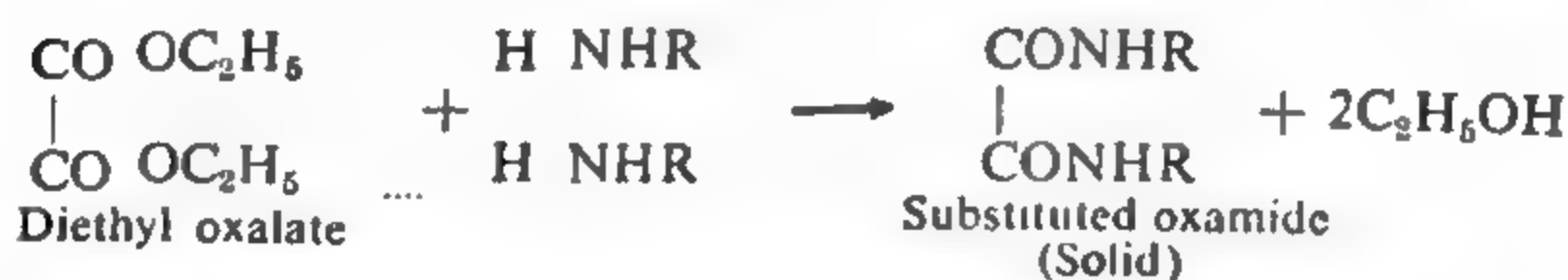
Separation of a Mixture of Amines

It has already been mentioned that by Hofmann's method or by the ammonolysis of alcohols invariably a mixture of primary, secondary and tertiary amines along with some quaternary compound is formed. Their separation is effected in the following manner.

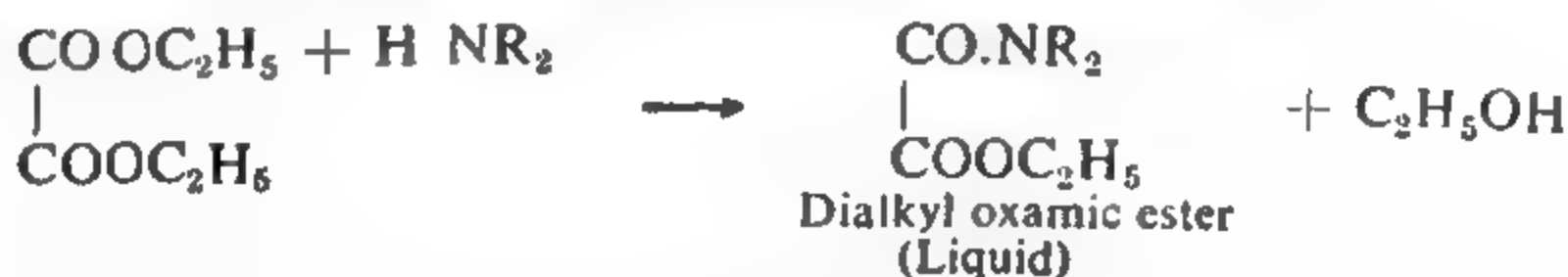
The mixture of the amines, along with the quaternary salt is distilled with potassium hydroxide. The three amines (primary, secondary and tertiary) distil over, leaving behind the non-volatile quaternary salt. The mixture of the three amines obtained in the distillate is separated into its constituents by either of the two methods discussed below :

(1) **Hofmann's Method.** The mixture of primary, secondary and tertiary amines is treated with diethyl oxalate, when the three amines react differently, as given below :

The primary amine forms a substituted amide (crystalline solid).

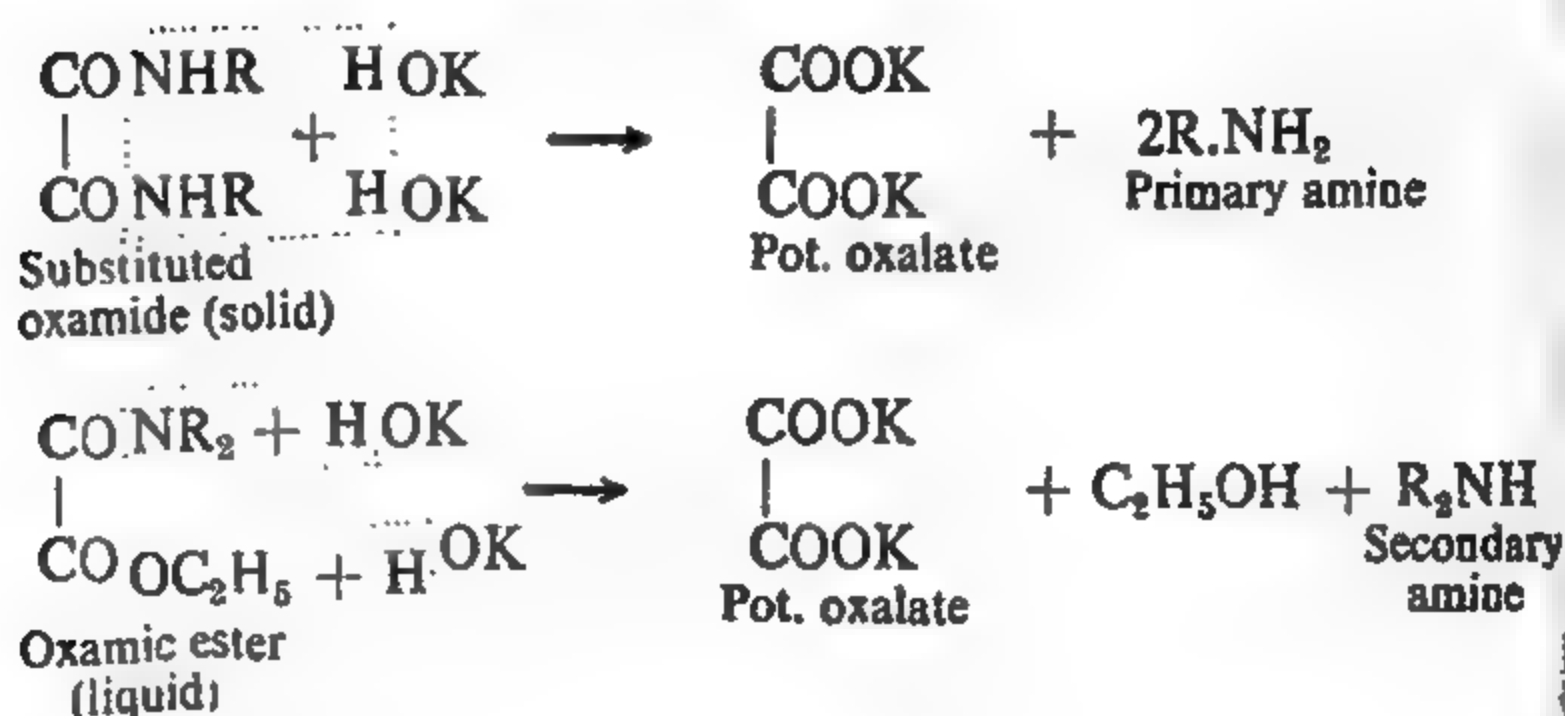


The secondary amine forms a dialkyl oxamic ester (liquid).



The tertiary amine, (R₃N), not containing a replaceable hydrogen atom, does not react at all.

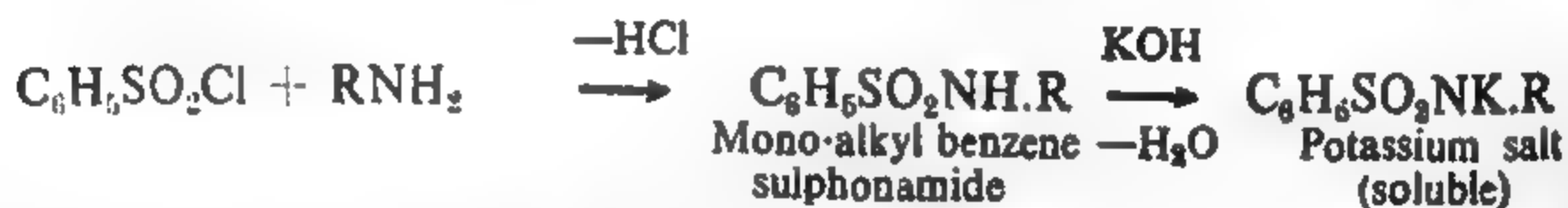
The mixture containing the substituted oxamide, oxamic ester, and unreacted tertiary amine is distilled, when the tertiary amine, being most volatile, distils over and is obtained in the distillate. The residual mixture in the distillation flask contains substituted oxamide (solid) and oxamic ester (liquid), and the two can be separated by simple filtration. The oxamide and oxamic ester are treated separately with strong alkali to regenerate the corresponding amines.



(2) **Hinsberg's Method.** This is a better method for the separation of amines.

(i) The mixture of primary, secondary and tertiary amines is treated with benzene sulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ (Hinsberg's reagent), when the following reactions take place :

A primary amine reacts to form a sulphonamide, which is soluble in alkali.



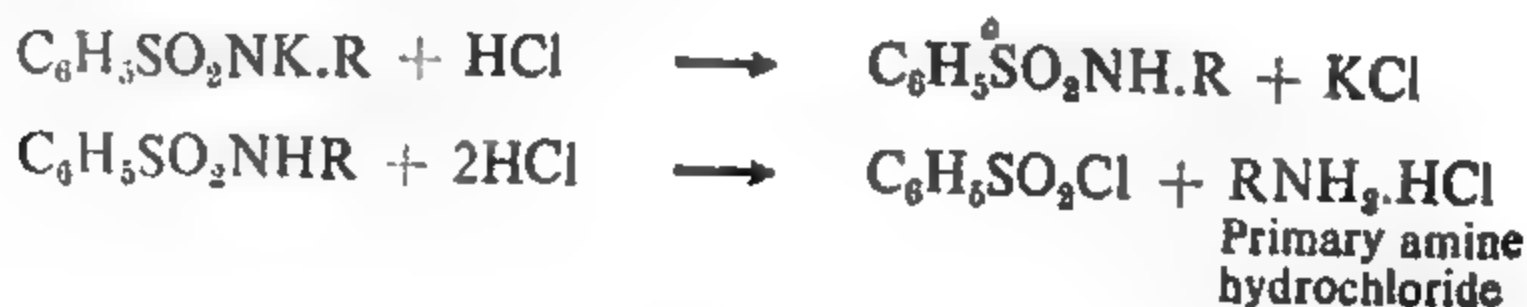
A secondary amine reacts to give a sulphonamide which is insoluble in alkali (as the sulphonamide does not contain a replaceable hydrogen attached to nitrogen).



A tertiary amine does not react at all.

(ii) After interaction with benzene sulphonyl chloride, the reaction mixture is treated with a 5% solution of potassium hydroxide and shaken with ether. The unreacted tertiary amine and the dialkyl benzene sulphonamide go into the ether layer whereas monoalkyl benzene sulphonamide remains in the aqueous layer in the form of its potassium salt. The two layers are separated.

(iii) The aqueous layer is treated with excess of hydrochloric acid when the potassium salt of the sulphonamide is decomposed giving the hydrochloride of primary amine.

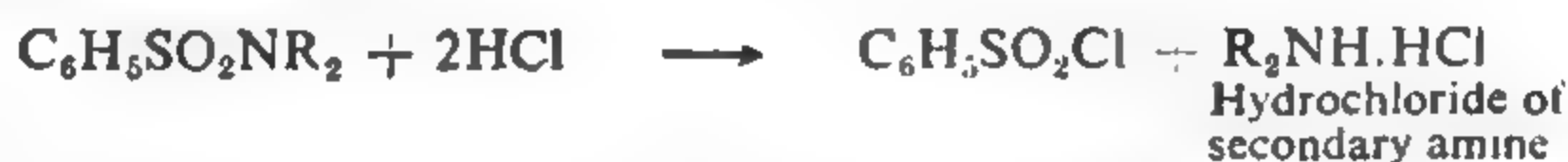


The hydrochloride is distilled with potassium hydroxide to recover the free primary amine.



(iv) The ethereal layer is distilled when the unreacted tertiary amine distils over along with ether.

The residue is treated with excess of hydrochloric acid when the dialkyl benzene sulphonamide is decomposed to give the hydrochloride of the secondary amine,



The hydrochloride is distilled with potassium hydroxide to liberate the free secondary amine.



(v) The ethereal solution of tertiary amine obtained above is fractionally distilled to separate the tertiary amine.

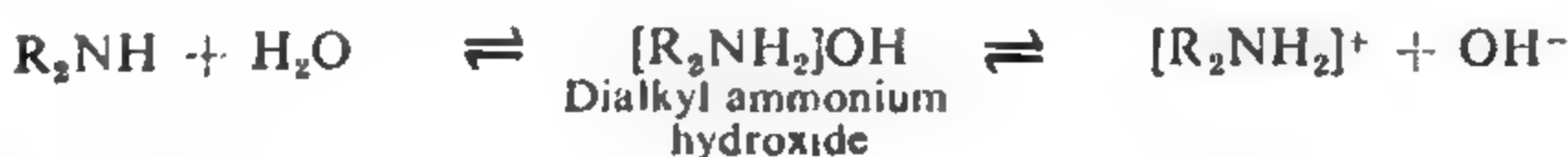
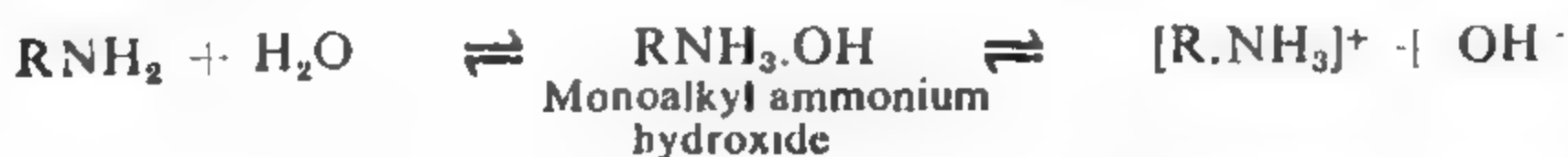
It is worth mentioning that now-a-days *p*-toluene sulphonyl chloride is used in place of benzene sulphonyl chloride as it works better.

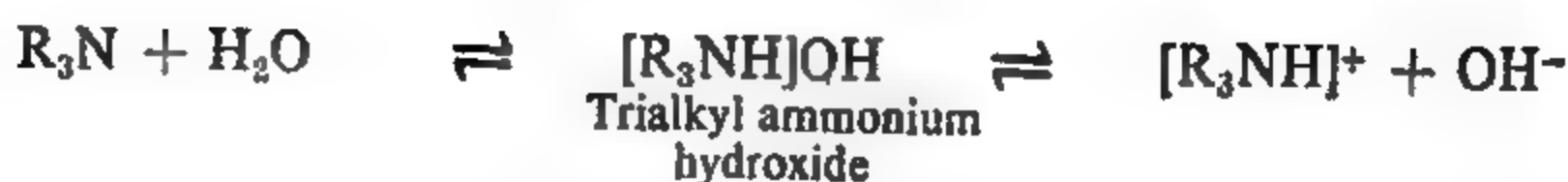
(3) Very recently, separation of amines by fractional distillation has been tried. Using highly efficient equipment, it has been possible to separate the three amines on a commercial scale.

Physical Properties. The lower members are gases with a fish-like ammoniacal odour which vanishes in higher members. The higher members are liquids and still higher ones are solids.

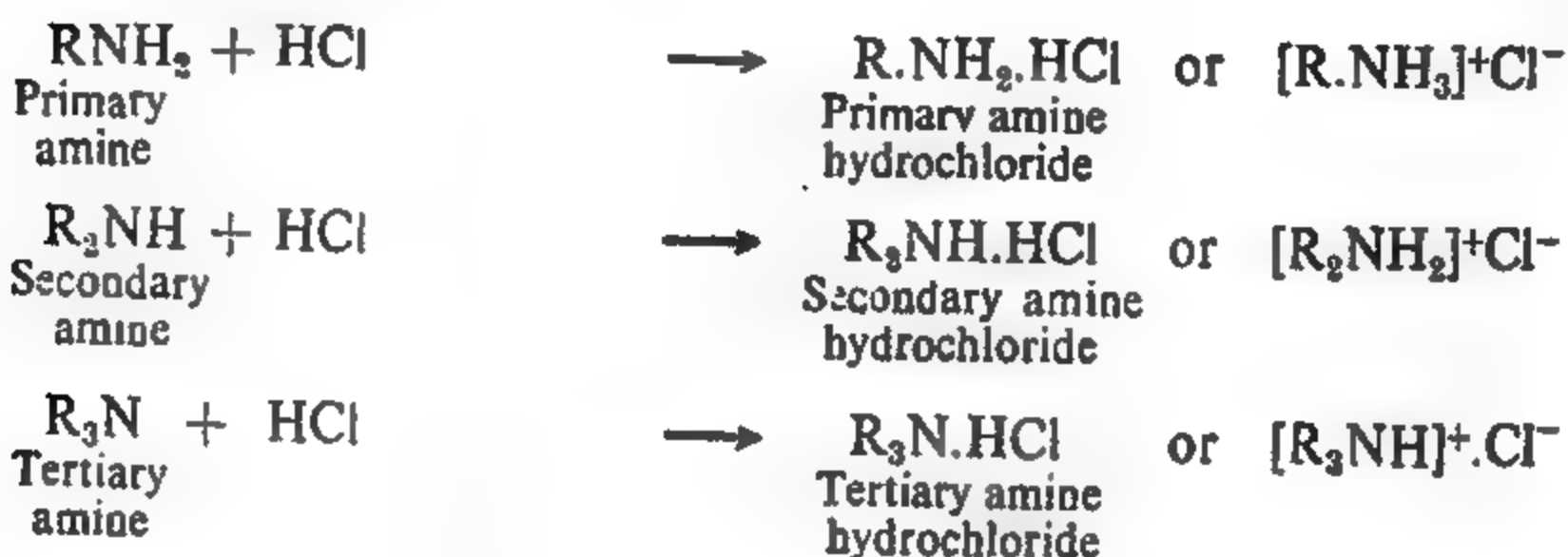
The lower members are soluble in water, but the solubility decreases with increase in molecular weight. The aqueous solutions of amines are strongly alkaline to litmus and conduct electricity.

Chemical Properties. (1) **Basic character.** Amines are strongly basic in character. When dissolved in water they furnish hydroxyl ions.



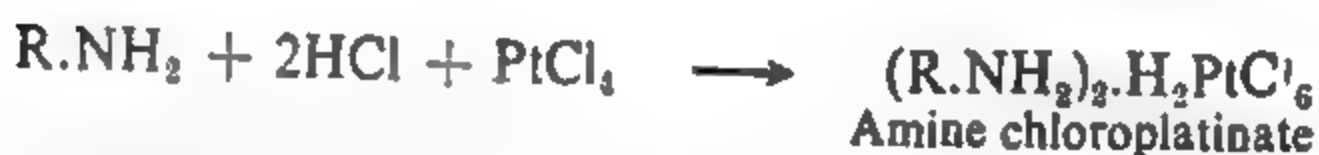


They form salts with acids :



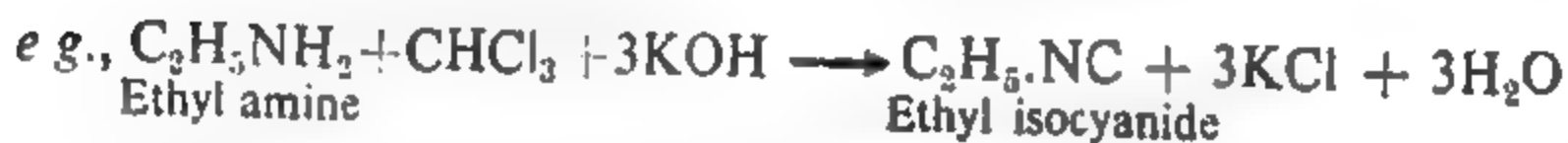
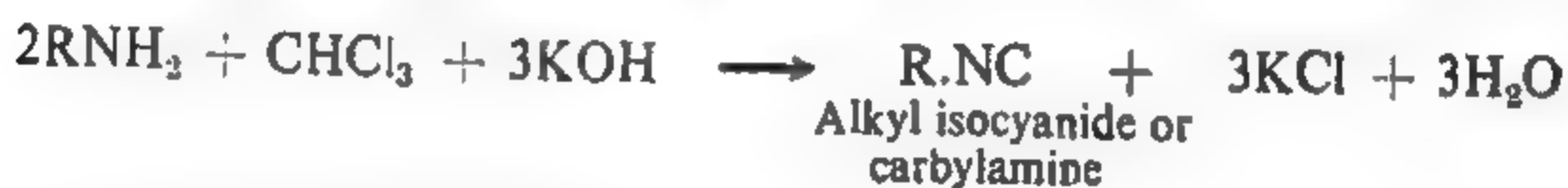
These salts are crystalline in nature, soluble in water and resemble the corresponding ammonium salts.

Amines form double salts with platinic chloride, PtCl_4 .



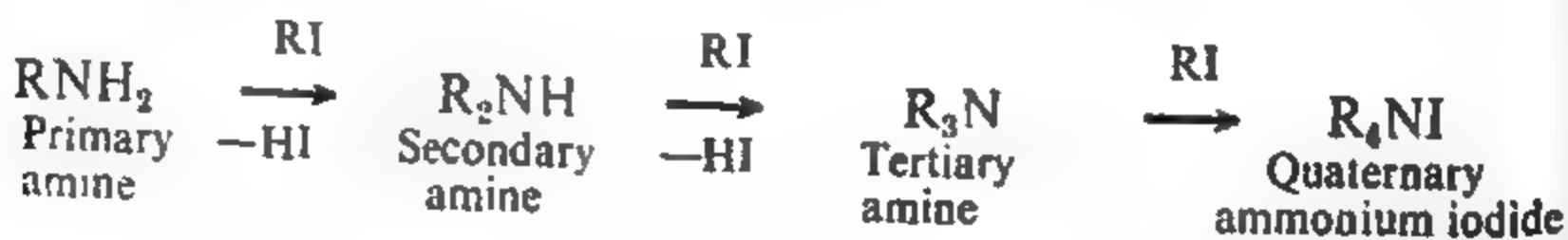
The platinichlorides or chloroplatinates decompose on strong ignition to yield pure platinum and this property is made use of in determining the molecular weight of organic bases (see chapter XXI).

(2) **Carbylamine reaction.** When warmed with chloroform and alcoholic potassium hydroxide, a primary amine forms an isocyanide or carbylamine which can be characterised by a highly unpleasant odour.

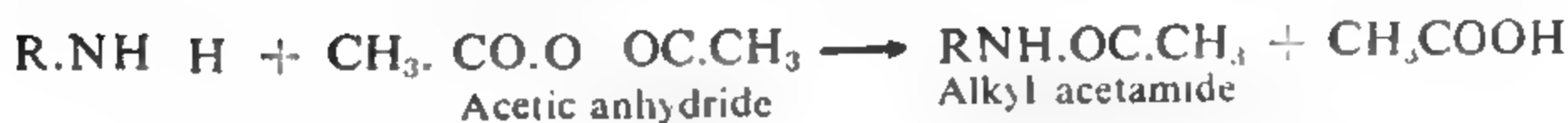


This reaction is not given by a secondary or a tertiary amine and is, therefore, used as a *test for primary amines*.

(3) **Reaction with alkyl halides.** Primary, secondary or tertiary amines react with alkyl halides to finally form the corresponding quaternary salts. Thus,



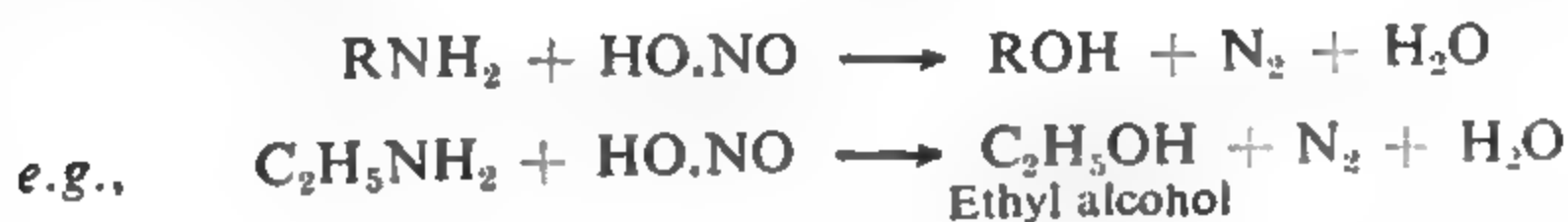
(4) **Acylation.** Primary and secondary amines (but not tertiary amines) react with acid chlorides or acid anhydrides, giving substituted amides.



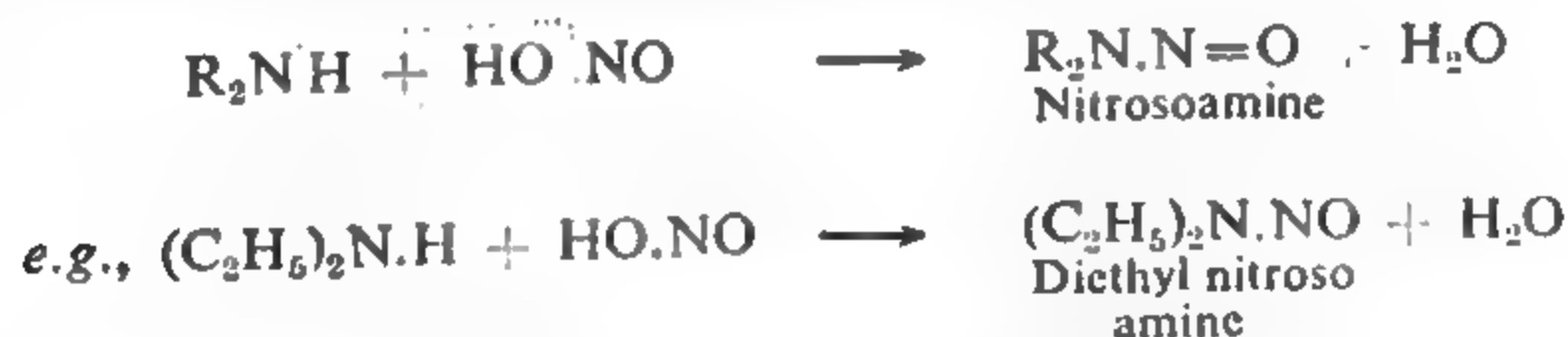
Tertiary amines do not contain any replaceable hydrogen and, therefore, do not react.

(5) **Reaction with nitrous acid.** Primary, secondary and tertiary amines behave differently in their action towards nitrous acid (*i.e.* $\text{NaNO}_2 + \text{dil HCl}$).

(a) Primary amines react readily to form an alcohol with the liberation of nitrogen*



(b) Secondary amines react slowly, yielding oily nitrosoamines which are characterised by Liebermann's test.



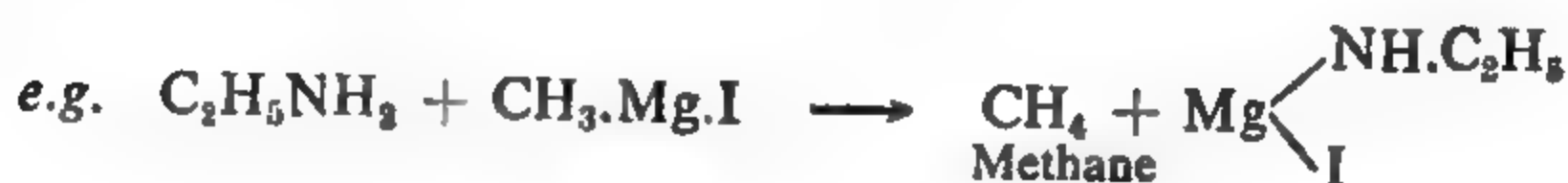
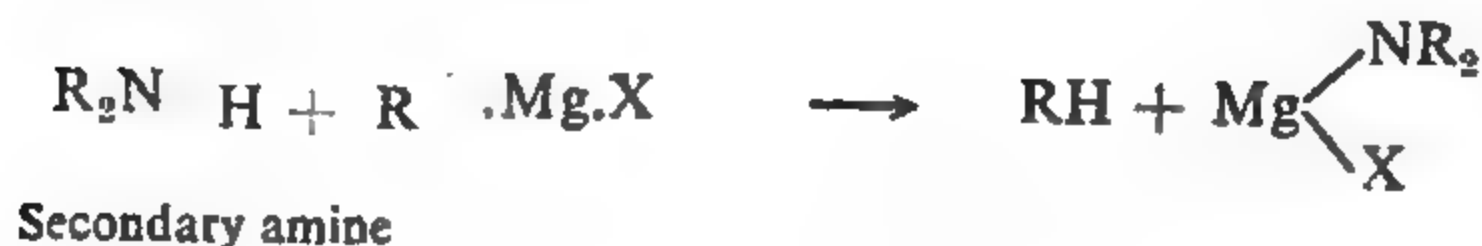
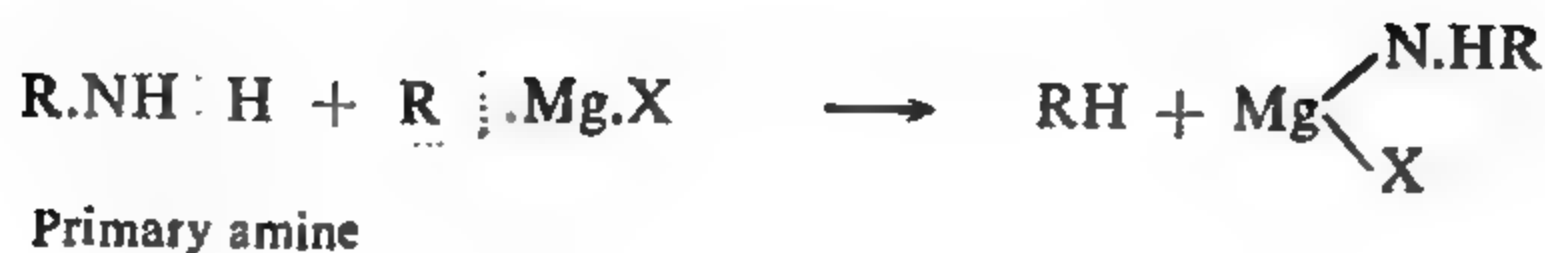
Lieberman's nitrosoamine reaction. The nitrosoamine is washed free of nitrous acid and warmed with a little phenol. On cooling and adding concentrated sulphuric acid, a greenish blue colour develops. On dilution with water the colour changes to red, but becomes greenish blue or violet again on addition of alkali.

Liebermann's nitrosoamine reaction is a delicate test for the identification of secondary amines.

Tertiary amines simply form salts with nitrous acid, *e.g.*, R_3NHNO_2 .

(6) **Action with Grignard reagents.** Primary and secondary amines react with Grignard reagents to give hydrocarbons. Tertiary amines have no reaction.

*The reaction is not so simple and straightforward. Several departures are known. For example, with methylamine, the main product is diethyl ether and not methyl alcohol. Ethylamine yields 60% of alcohol and *n*-propylamine yields propyl and isopropyl alcohols.



Distinction between Primary, Secondary and Tertiary Amines.

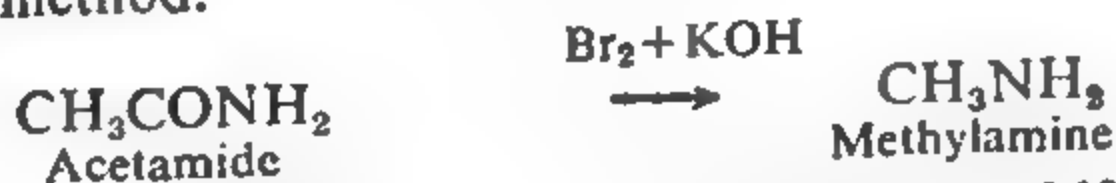
The various tests which can be employed to distinguish between primary, secondary and tertiary amines are given in the following table :

Test	Primary amine	Secondary amine	Tertiary amine
1. Action with alkyl halide	Combines with 3 molecules of halide to form the quaternary salt.	Combines with 2 molecules to form the quaternary salt.	Combines with one molecule to form the quaternary salt.
2. Action with acetyl chloride	Forms acetyl derivative.	Forms acetyl derivative.	No action.
3. Action with nitrous acid	Forms an alcohol.	Forms a nitroso-amine characterised by Liebermann's test.	Forms a nitrite.
4. Carbylamine test.	Forms a carbylamine with a disgusting odour.	No action.	No action
5. Action with Grignard reagent.	Forms a hydrocarbon.	Forms a hydrocarbon.	No action
6. Action with Hinsberg's reagent. $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$	Yields sulphonamide, soluble in alkali.	Yields sulphonamide, insoluble in alkali.	No action.

INDIVIDUAL MEMBERS

METHYLAMINE, CH_3NH_2

Methylamine is the simplest representative amine, which can be prepared by any of the methods of preparation discussed earlier. However, it is most conveniently obtained in the laboratory by Hofmann's bromamide method.

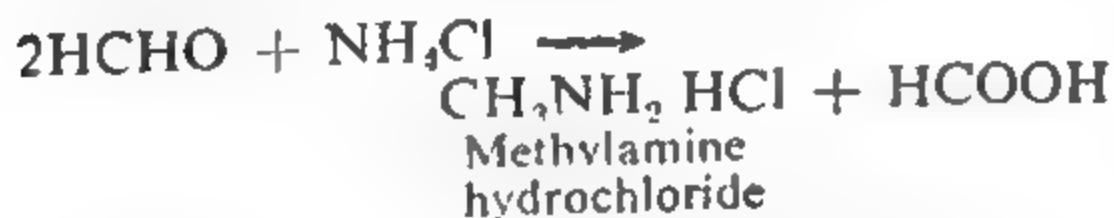


Laboratory Preparation. Take 12 gm. of acetamide and 10.8 c.c. of bromine in a round bottomed flask and run in 10% KOH solution with constant shaking and cooling under tap, till the reaction mixture becomes pale yellow. This indicates the formation of bromoacetamide.

Fit up an apparatus as shown in Fig. 1. Take a concentrated solution of 36 gm. of potassium hydroxide in 60 c.c. of water in the flask and heat gently until a temperature of $60-70^\circ$ is registered (thermometer not shown in the Fig.). At this stage, add bromoacetamide solution from the dropping funnel at such a rate that the temperature does not exceed 70° . Heat for ten minutes more, after the addition of bromoacetamide is over. The reaction mixture is now colourless.

Distil the solution and pass the vapour of methylamine, along with steam, into a beaker containing dilute hydrochloric acid. In about 30 minutes, the evolution of methylamine is complete. The solution of methylamine hydrochloride is evaporated to a solid mass, from which the free amine may be regenerated by distillation with an excess of alkali.

(2) On an industrial scale, methylamine is prepared by warming a mixture of ammonium chloride and formalin (formaldehyde dissolved in water).



Free methylamine may be obtained by boiling the reaction mixture with strong sodium hydroxide solution.

Properties. Methylamine is a colourless gas with a strong ammonia-like odour. It burns in air with a yellow flame. Like ammonia, it is also highly soluble in water. On intense cooling, it yields a liquid boiling at -6° .

Chemically, it is a typical primary amine and gives all the reactions mentioned earlier. It is used as a refrigerant.

Ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$

Ethylamine, like methylamine, can be prepared by any of the general methods of preparation for primary amines. (cf. summary on page 502).

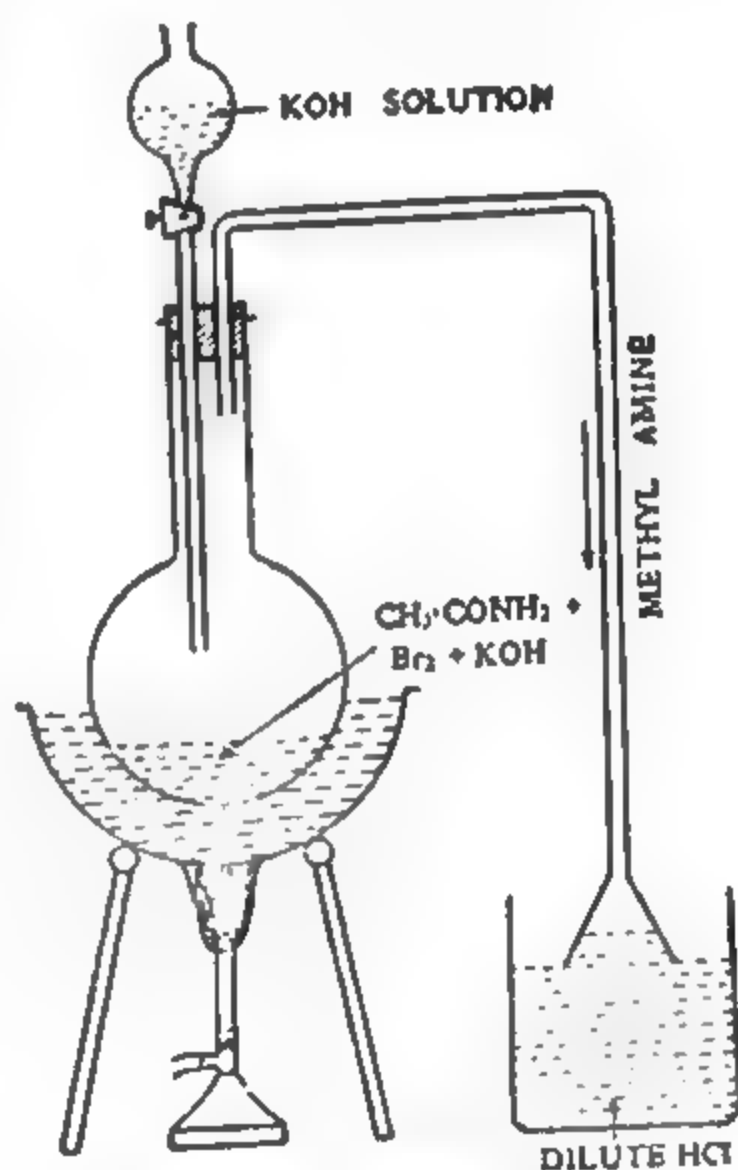
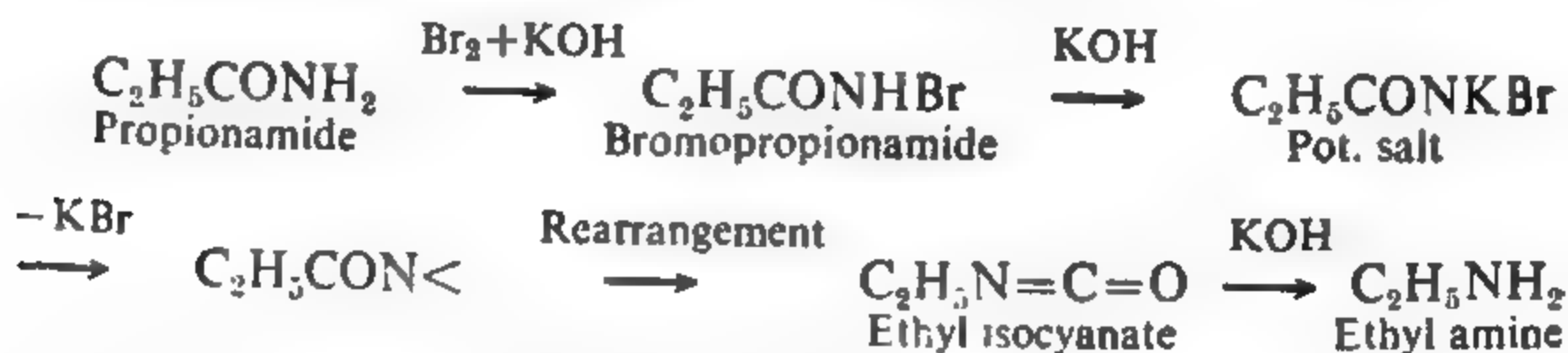


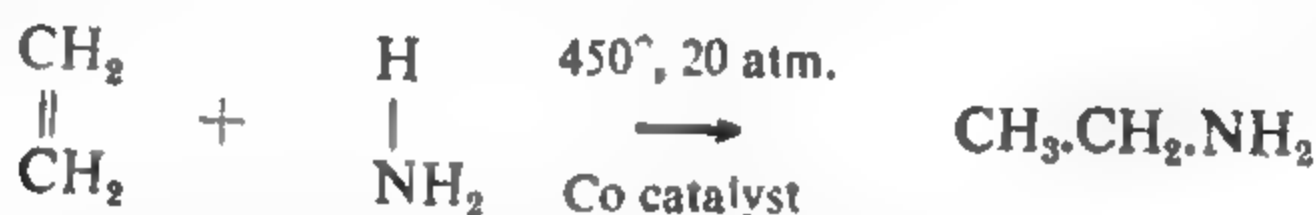
Fig 1. Preparation of Methylamine.

(2) Ethyl amine is prepared in laboratory by Hofmann's bromamide reaction, using propionamide in place of acetamide.



The apparatus and the details of the experiment are essentially the same as in the laboratory preparation of methyl amine discussed above.

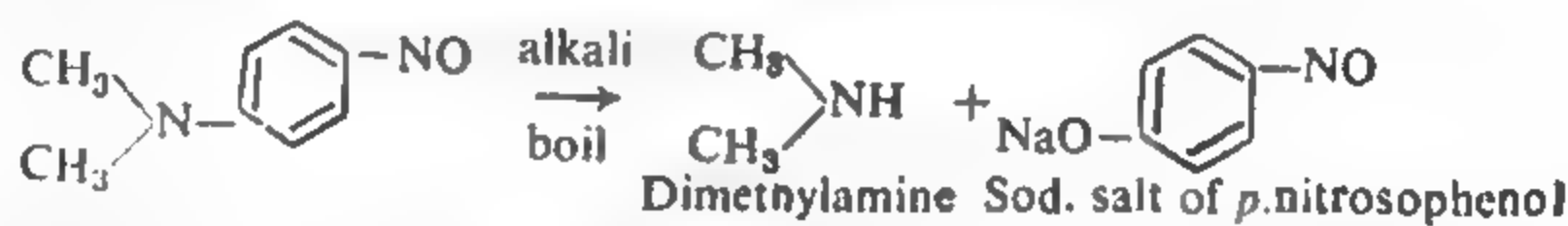
(3) On a large scale it is prepared by passing a mixture of ethylene and ammonia over a cobalt catalyst at 450° and under 20 atmospheres of pressure.



Ethylamine is a colourless liquid (b.p. 19°), with an ammoniacal odour. It is highly soluble in water. It burns with a yellow flame. It gives all the reactions of primary amines (cf. summary on page 503)

Dimethylamine. $(\text{CH}_3)_2\text{NH}$

Dimethylamine is the simplest secondary amine and is best prepared by the hydrolysis of *p*-nitroso-dimethylaniline with alkali.



Dimethylamine is a colourless liquid boiling at 7° and having an ammoniacal odour. It is a typical secondary amine. It is employed for debairing of hides and as an accelerator in the vulcanisation of rubber.

Trimethylamine. $(\text{CH}_3)_3\text{N}$

Trimethylamine is the simplest tertiary amine. It occurs naturally in the excreta of fish and in some plants (*hawthorn blossom*).

Industrially, it is formed by the destructive distillation of beet sugar molasses. In laboratory, it is obtained by the decomposition of tetramethyl ammonium hydroxide.



It is a colourless liquid boiling at 3.5° . It is commercially employed for the preparation of methyl chloride by heating it at 360° with hydrochloric acid.



Ascent and Descent of Series

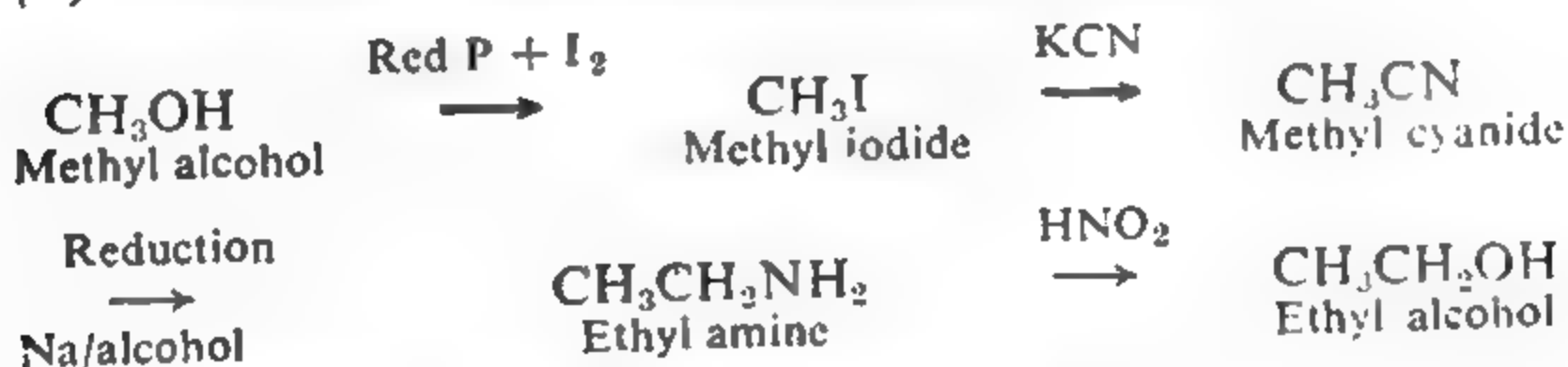
It would be of interest to note that ascent in homologous series can be achieved through interaction between alkyl halide and potassium cyanide when an alkyl cyanide is formed, which contains one carbon atom more than the alkyl halide.

The descent in a homologous series can be brought about by Hofmann's bromamide degradation, in which an acid amide on treatment with bromine and potassium hydroxide results in the formation of an amine which contains one carbon atom less than the amide.

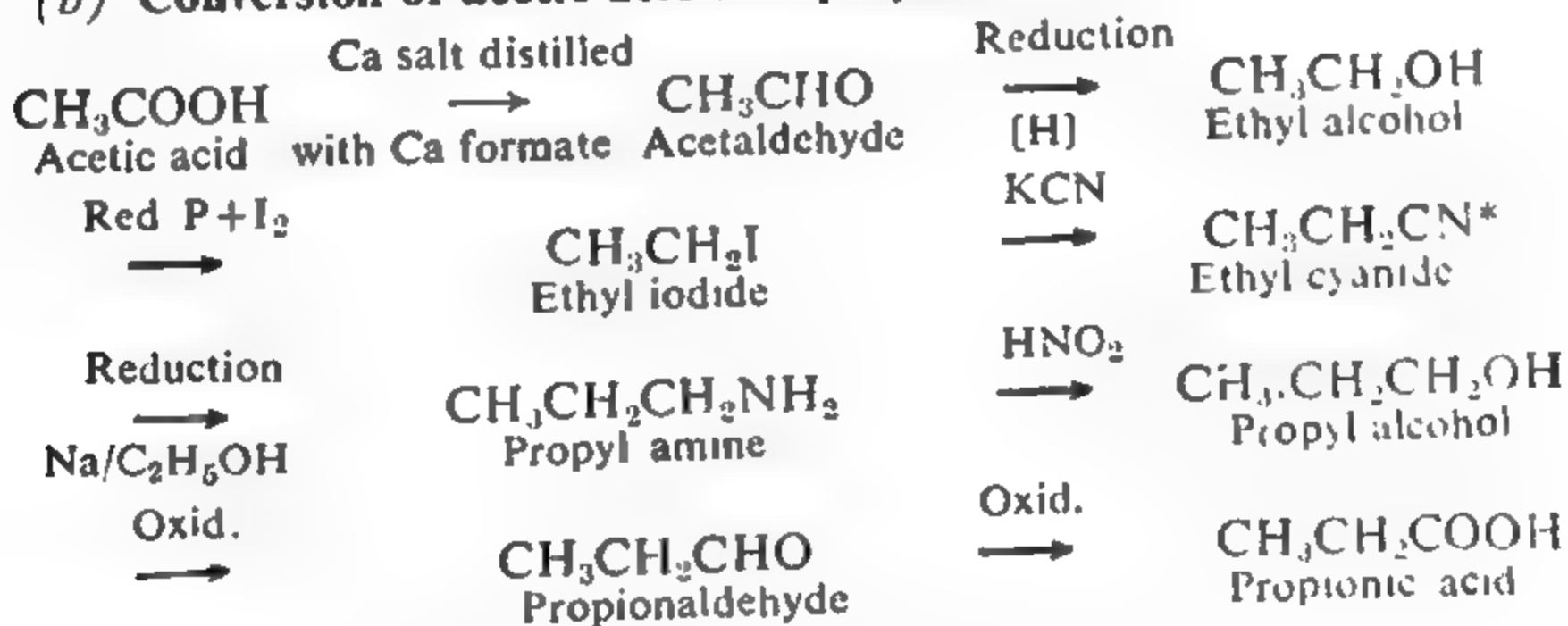
A few examples will illustrate the above points.

Ascent in Series.

(a) Conversion of methyl alcohol into ethyl alcohol.

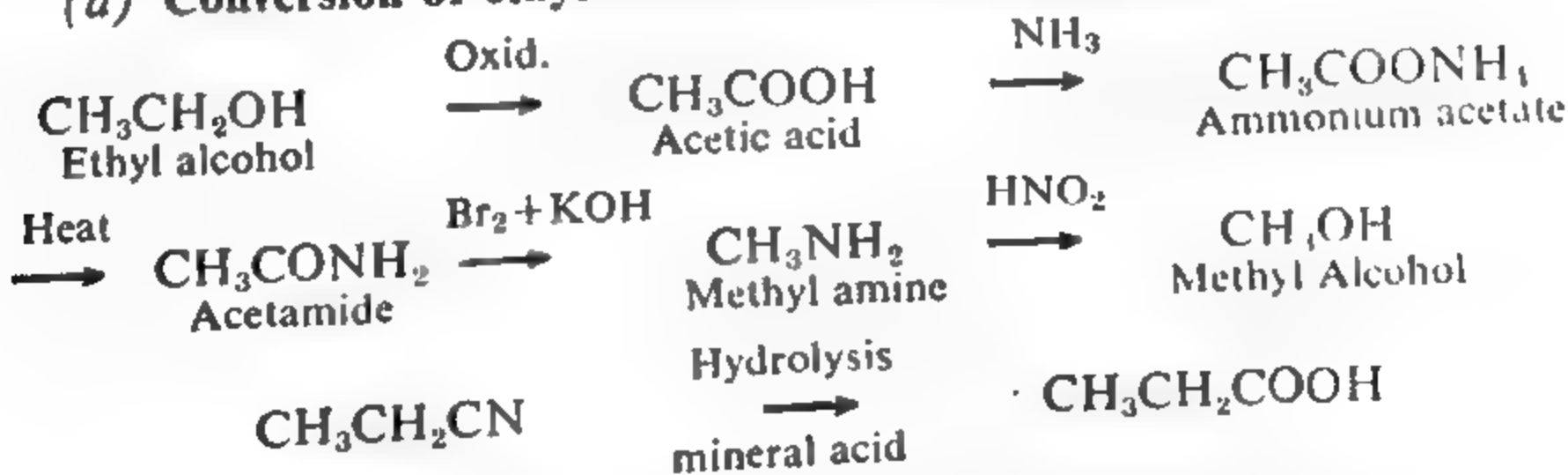


(b) Conversion of acetic acid into propionic acid.



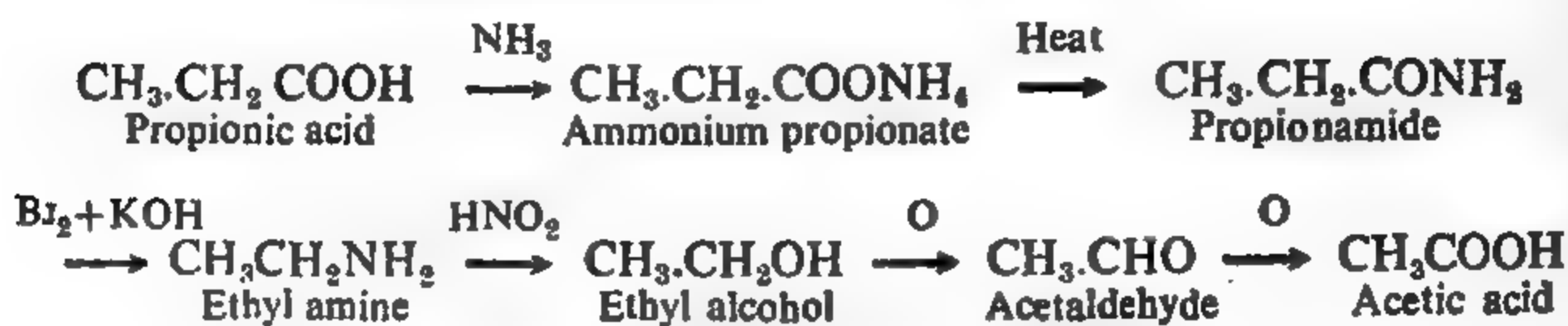
Descent in Series.

(a) Conversion of ethyl alcohol into methyl alcohol.



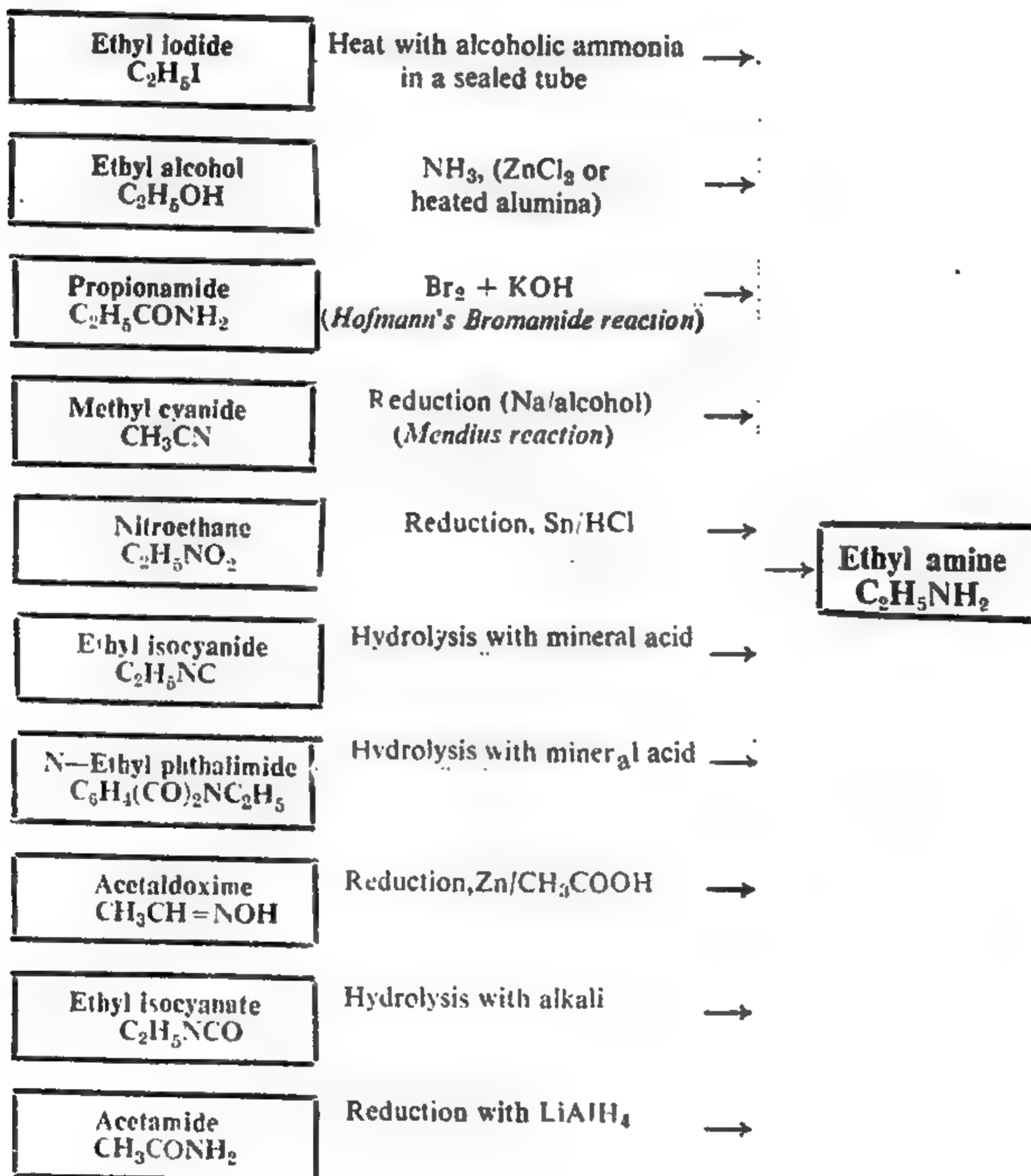
*Ethyl cyanide can be converted into propionic acid in one step, by hydrolysis.

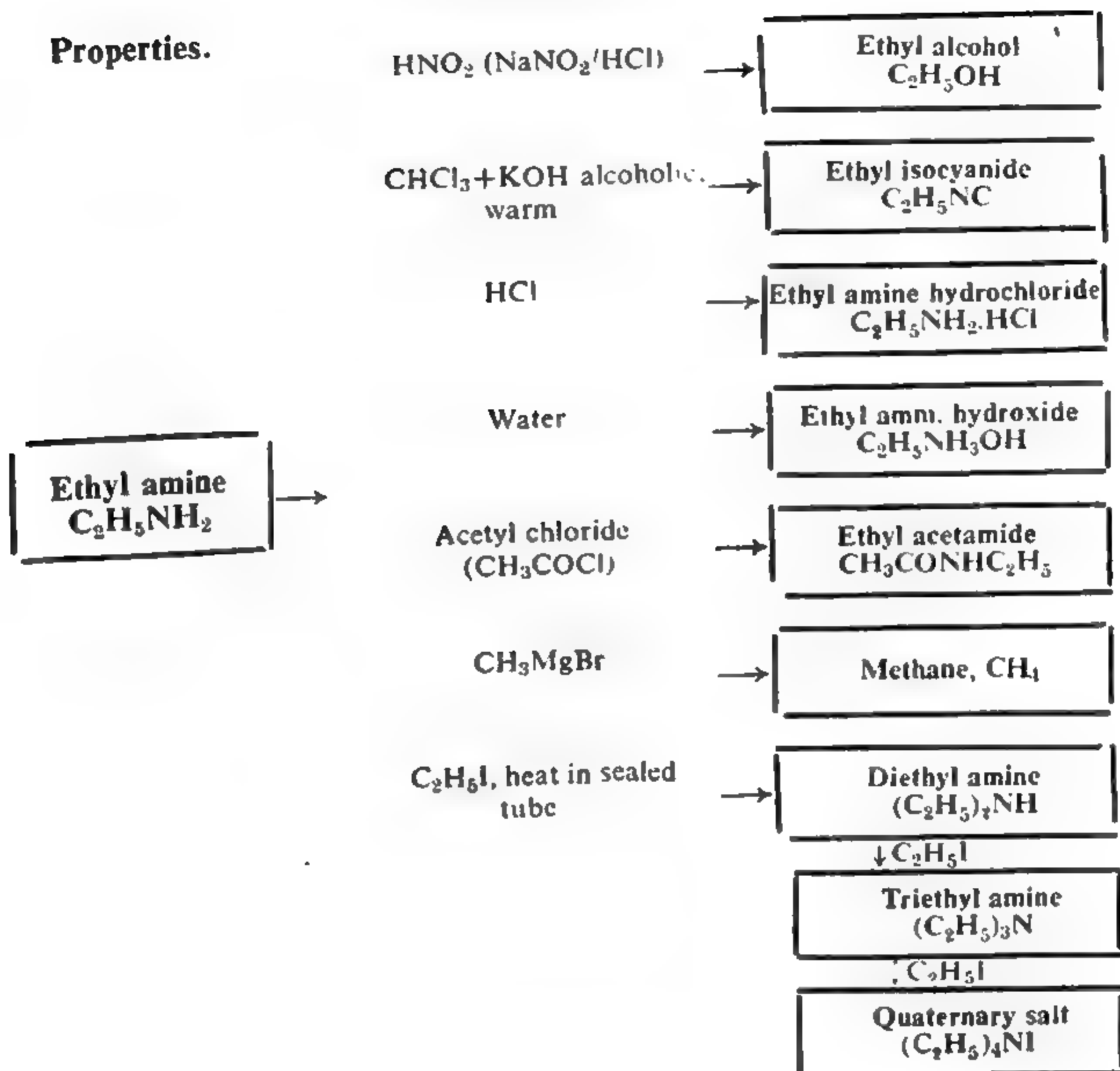
(b) Conversion of propionic acid into acetic acid.



SUMMARY OF A TYPICAL MEMBER

Preparation.



Properties.**QUESTIONS**

1. What are amines? How are they classified? What are their characteristic groups? Illustrate your answer with examples.
2. Describe the general methods of preparation of the various types of amines.
3. How will you separate a mixture of primary, secondary and tertiary amines? Give chemical reactions involved.
4. How does methylamine react with :
(a) Nitrous acid (b) Methyl iodide (c) Acetic anhydride (d) Ethyl magnesium iodide (e) Chloroform and potassium hydroxide (f) Bromine and KOH?
5. What happens when :
(a) Ethyl amine is heated with ethyl bromide in a sealed tube (b) Trimethylamine is heated with ethyl iodide (c) Tetramethyl ammonium hydroxide is distilled (d) Acetamide is heated with sodium hypobromite (e) Trimethylamine is heated with hydrochloric acid?
6. Write short notes on :
(a) Hofmann's bromamide degradation (b) Hinsberg's method for the separation of amines (c) Libermann's nitrosoamine test (d) Mendius reduction.

7. How will you distinguish between a primary, secondary and a tertiary amine? Give the chemistry involved.

8. How will you prepare a sample of methylamine in laboratory? What are its properties?

How will you determine the molecular weight of the compound?

9. Write equations indicating the reagents used and conditions employed for :

(a) Reduction of an alkyl cyanide (b) Reduction of a nitroparaffin (c) Hydrolysis of *p*-nitroso diethylaniline (d) Hydrolysis of *N*-ethyl phthalimide (e) Reduction of an isonitrile (f) Reduction of an oxime.

10. How will you convert :

(a) Methyl alcohol into ethyl alcohol and *vice versa* (b) Acetic acid into propionic acid and *vice versa* (c) Ethylamine into methylamine and *vice versa*?

11. Write short notes on :

(i) Ascent and Descent in Homologous Series.

(ii) Isomerism in amines.

(iii) Nomenclature of amines.

12. Present a scheme by which Methylamine and Ethylamine can be converted into each other. (Panjab Inter 1961, 54)

13. Describe in each case two reactions associated with the presence of the following groups in the molecule of the organic compounds : (i) $-\text{CONH}_2$ (ii) $-\text{CH}_2\text{NH}_2$. (Panjab Inter 1960)

14. (a) Describe Hinsberg's method for separating primary, secondary and tertiary amines. (Panjab Inter 1959 S)

(b) Write illustrative but brief note on : Descent of a homologous series.

(Panjab Inter 1959 S)

15. Outline a scheme for preparing propionic acid starting from methyl alcohol.

(Panjab Inter 1957)

16. What are amines? Give examples of the different classes of amines.

Given a mixture of the different classes of amines, how would you proceed to separate them from one another and show which is which? (Panjab Inter 1957)

17. NaOH is an inorganic base. Mention at least one organic substance which exhibits similar properties. Give the preparation, other important properties and distinctive tests of substance selected. (Panjab Inter 1952 S)

18. How can you obtain ethylamine in a reasonably pure form from two different sources? Differentiate this amine from diethylamine, triethylamine and methylamine.

(Panjab Inter 1951)

19. How are alkyl derivatives of ammonia named and classified? Give any two methods for their preparation and say how the different classes can be distinguished.

(Panjab Inter 1949)

20. Give the tests by which primary, secondary and tertiary amines can be distinguished from one another. How will you get methylamine from acetic acid?

(Panjab B.Sc. Part I 1962)

21. How will you convert methylamine into ethylamine and *vice versa*. Describe each step and illustrate it by proper equations.

(Ajmer Inter 1951)

22. What are the general methods for the preparation of amines? Show how you can distinguish between the primary, secondary and tertiary amines.

(Jammu & Kashmir Inter 1958)

CHAPTER XLI

CARBOHYDRATES

The Carbohydrates. The carbohydrates constitute a very large number of naturally occurring compounds, such as glucose $C_6H_{12}O_6$, fructose $C_6H_{12}O_6$, cane-sugar $C_{12}H_{22}O_{11}$, cellulose, starch $(C_6H_{10}O_5)_n$, etc. All the carbohydrates are made up of carbon, hydrogen and oxygen and each one of these could be represented by the general formula $C_x(H_2O)_y$. The carbohydrates could thus, be regarded as 'hydrates of carbon' (cf. inorganic hydrates, such as $CuSO_4.5H_2O$, $FeSO_4.7H_2O$, $Na_2SO_4.10H_2O$).

But the above definition of carbohydrates was found to be inherently wrong because :

(i) Carbon is not known to form 'hydrates' as the term is understood in inorganic chemistry.

(ii) Some compounds, such as *rahnose* and *fucose*, $C_6H_{12}O_5$, were isolated and studied, which definitely belonged to the class of carbohydrates, but still their formulae could not correspond to the general formula, $C_x(H_2O)_y$.

(iii) Such organic compounds of carbon, hydrogen and oxygen are known, in which hydrogen and oxygen are present in the same proportion as in water (e.g., formaldehyde, CH_2O ; acetic acid, $C_2H_4O_2$; lactic acid $C_3H_6O_3$, etc.) but none of them could be regarded as 'carbohydrate.' Hence, another definition has been suggested and accepted. According to modern views, **carbohydrates are either aldehydic alcohols or ketonic alcohols.** For example, glucose and fructose are aldehydic alcohol and ketonic alcohol respectively.

Classification and Nomenclature. In general, the carbohydrates belong to two classes :

(a) *Sugars.* These are crystalline, soluble in water and are sweet in taste. Examples of this type are glucose, cane-sugar, fructose.

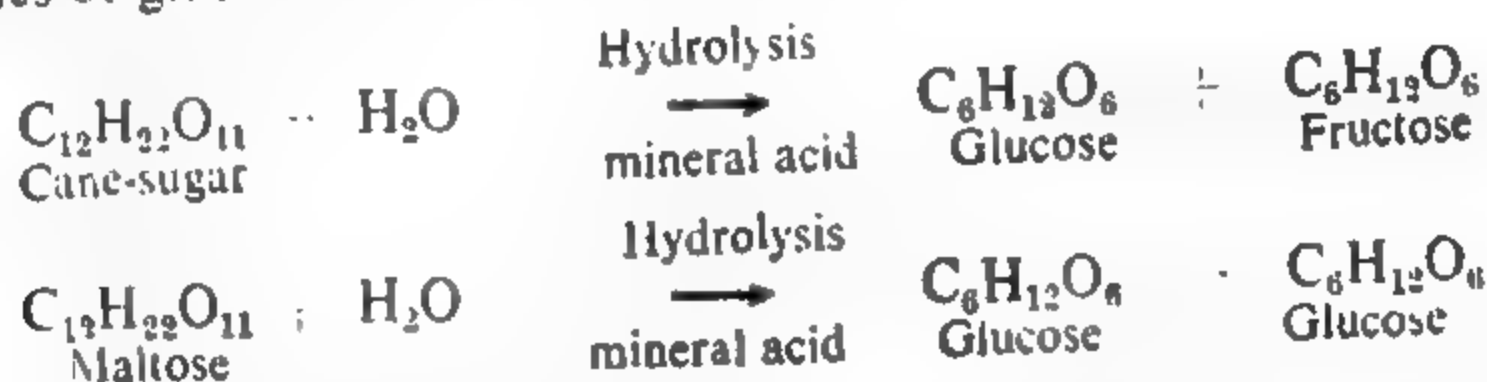
(b) *Non-sugars.* These carbohydrates are amorphous, insoluble in water and tasteless. Starch, cellulose, gum are examples of this type.

But the above classification is not a scientific one. A more rational classification has been evolved. It is based upon the number of carbon

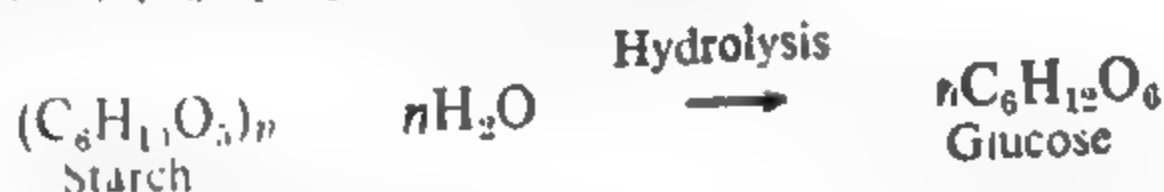
atoms in a molecule of a carbohydrate and the number of simpler units which it can give on hydrolysis.

(1) *Carbohydrates, which contain up to six carbon atoms in a molecule and do not hydrolyse to give simpler units, are called monosaccharides.* For example, glucose $C_6H_{12}O_6$, fructose $C_6H_{12}O_6$, arabinose $C_5H_{10}O_5$, etc., are all monosaccharides. They are of two types: *ketonic alcohols and aldehydic alcohols.* For instance, glucose, $CH_2OH.(CHOH)_4.CHO$, is an aldehydic alcohol and fructose, $CH_2OH.CO.(CHOH)_3.CH_2OH$, is a ketonic alcohol. The carbohydrates end in *-ose* and generally a Greek letter showing the number of carbon atoms in the molecule of a carbohydrate is prefixed, e.g., glucose, $CH_2OH.(CHOH)_4.CHO$, is an aldohexose and fructose, $CH_2OH.(CHOH)_3.CO.CH_2OH$, is a ketohexose.

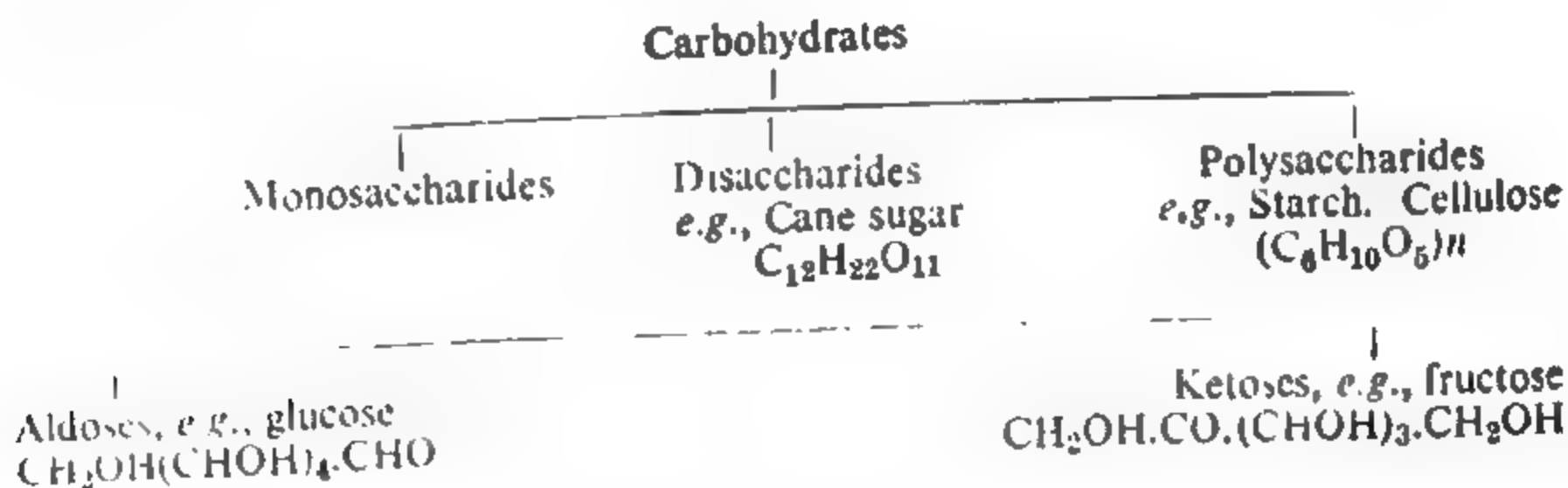
(2) *Carbohydrates, which contain twelve carbon atoms in a molecule and which on hydrolysis yield two monosaccharide molecules, are known as disaccharides.* Cane-sugar, lactose, maltose (all having the formula, $C_{12}H_{22}O_{11}$) are such examples. Cane-sugar, on hydrolysis, yields glucose and fructose molecules and maltose on similar treatment gives two molecules of glucose.



(3) *Carbohydrates, which on hydrolysis yield three or more molecules of monosaccharides, are called polysaccharides.* Starch, cellulose and dextrin, $(C_6H_{10}O_5)_n$, are such examples.



The above classification of carbohydrates may be summed up as under :



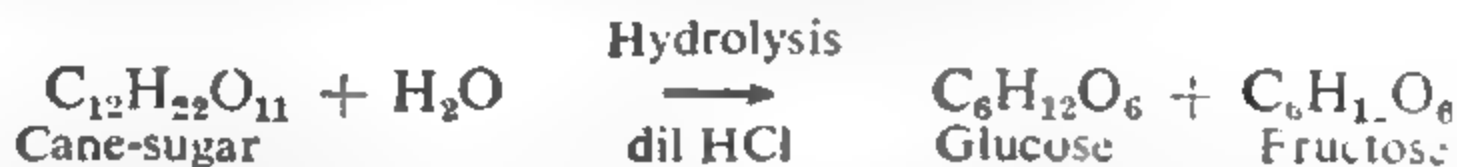
MONOSACCHARIDES

GLUCOSE, GRAPE SUGAR, DEXTROSE, $C_6H_{12}O_6$

Glucose is by far the most important monosaccharide. It occurs widely in seeds and leaves of plants, fruits and in honey. Ripe grapes

may contain up to 20% of glucose, hence the name *grape sugar*. It is also present in the blood normally within the range 0.08%—0.18% by weight, but in diabetic patients the glucose content may rise up to 0.3% in blood and much higher in urine.

Preparation. (1) Glucose is prepared by hydrolysis of cane-sugar with dilute hydrochloric acid in 90% alcohol solution.



Glucose being less soluble in alcohol crystallises out leaving behind the more soluble fructose in the mother liquor. It is filtered and recrystallised from dilute alcohol.

(2) **Manufacture.** (a) **From starch.** Industrially, glucose is prepared by hydrolysis of starch with dilute sulphuric acid. The starchy material like maize, rice, or potatoes is heated with dilute sulphuric acid under 3 atmospheres pressure. After the hydrolysis is complete, the excess of the acid is neutralized with chalk (CaCO_3) and the insoluble CaSO_4 is filtered out. The filtrate is decolorised with animal charcoal and then evaporated in vacuum when glucose crystallises out as monohydrate, $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$. The crude product always contains dextrin as an impurity which is got rid of by recrystallisation from alcohol.

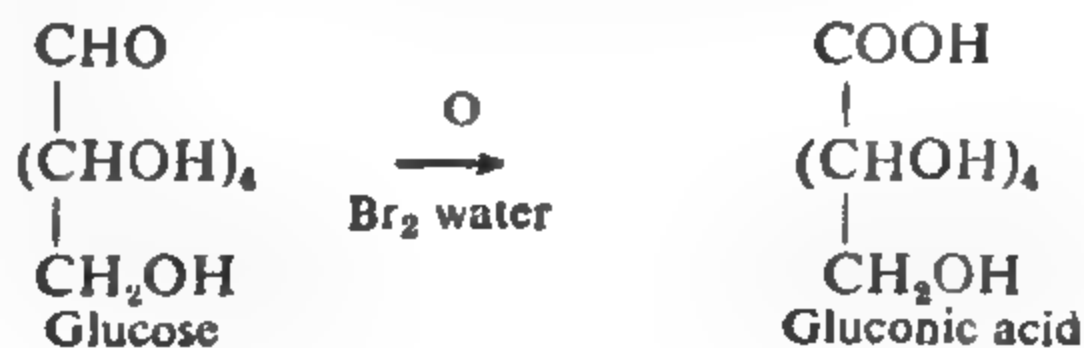
(b) **From cellulose.** Now-a-days, glucose is obtained by hydrolysis of wood cellulose with dilute acid under pressure till the hydrolysis is complete. The excess of the acid is removed with chalk and glucose obtained by the same process as above.

Physical Properties. Glucose is a crystalline sweet substance, soluble in water, insoluble in alcohol and ether. It crystallises from water as monohydrate (m.p. 83°) and from alcohol in anhydrous state (m.p. 146°). Its aqueous solution is optically active and is dextro-rotatory, hence, the name **dextrose**.

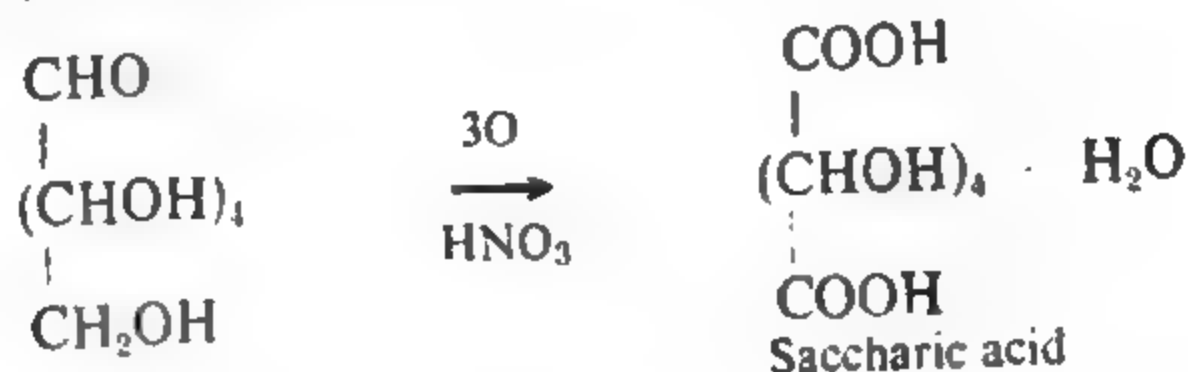
Glucose has the structure $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CHO}$. It contains one aldehydic and five hydroxyl groups. Glucose, therefore, combines the properties of an aldehyde and a polyhydric alcohol.

(a) **Reactions of aldehydic group.**

(i) **Oxidation** (a) With a mild oxidising agent like bromine water, glucose is oxidised to *gluconic acid*.

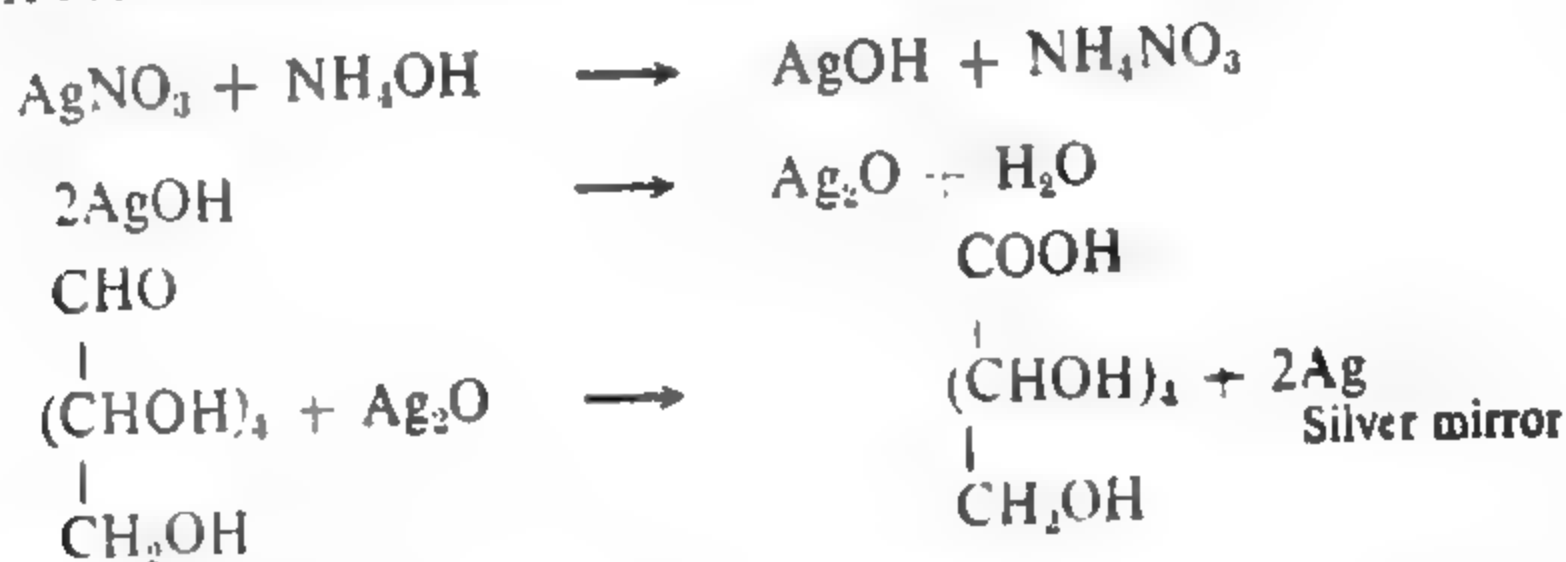


(b) With a strong oxidising agent like nitric acid. *saccharic acid*, a dicarboxylic acid, is obtained.

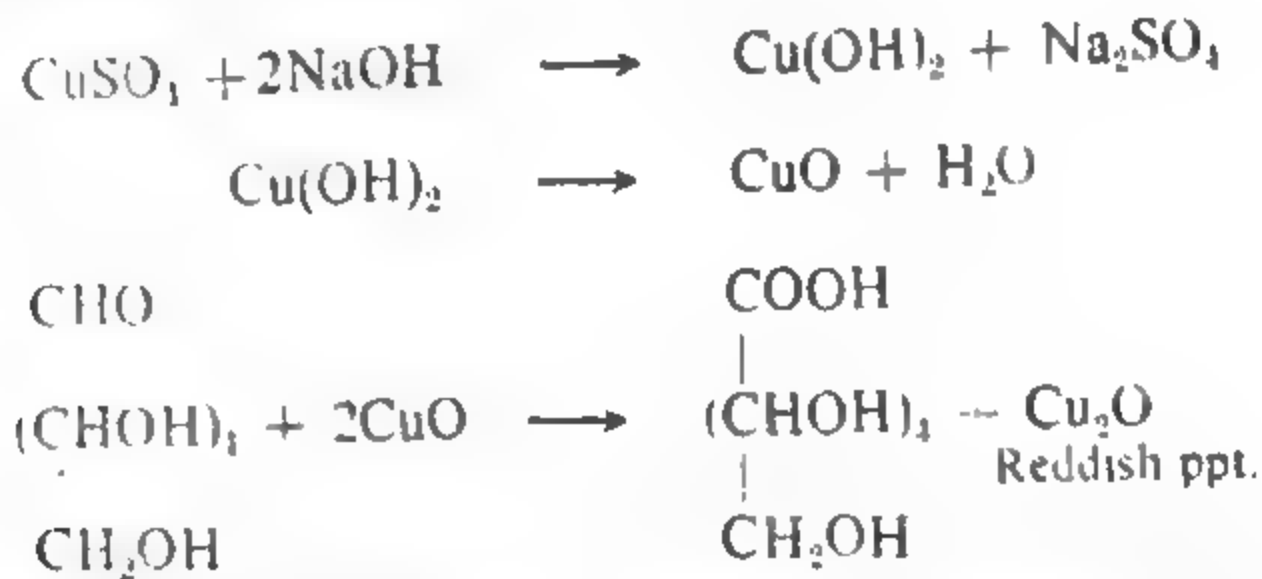


(ii) **Reducing properties.** Since glucose can be easily oxidised to gluconic acid, it acts as a reducing agent.

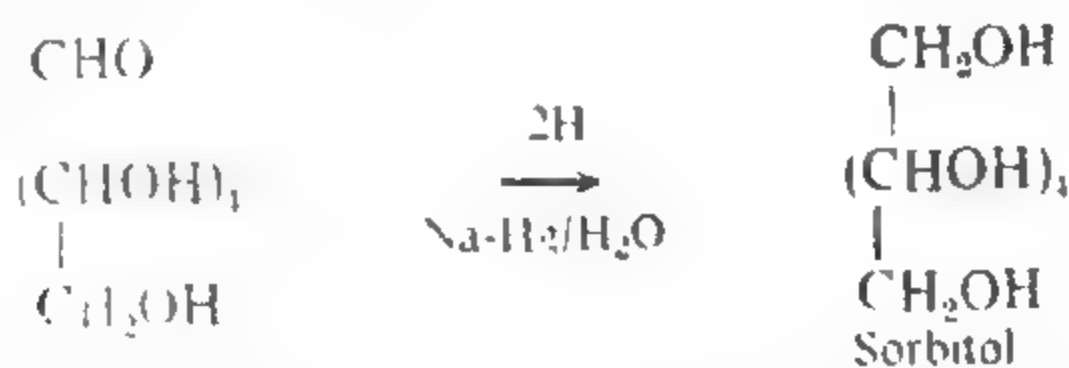
(a) It reduces ammoniacal silver nitrate to metallic silver.



(b) It reduces Fehling solution*, i.e., alkaline copper sulphate to red cuprous oxide.

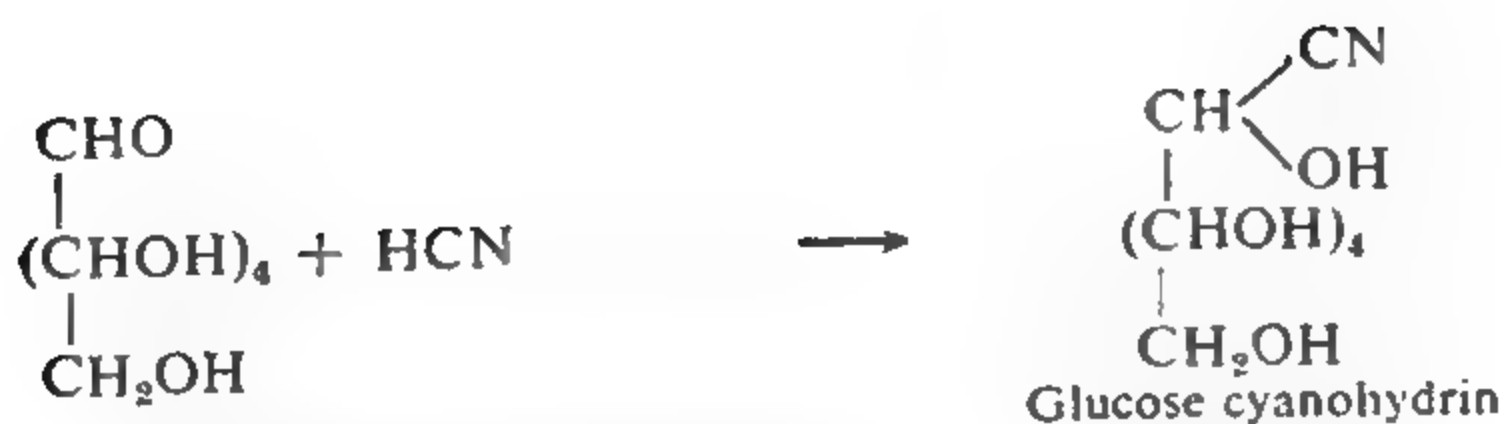


(iii) **Reduction.** On reduction with sodium amalgam, glucose yields *sorbitol*, a hexahydric alcohol.

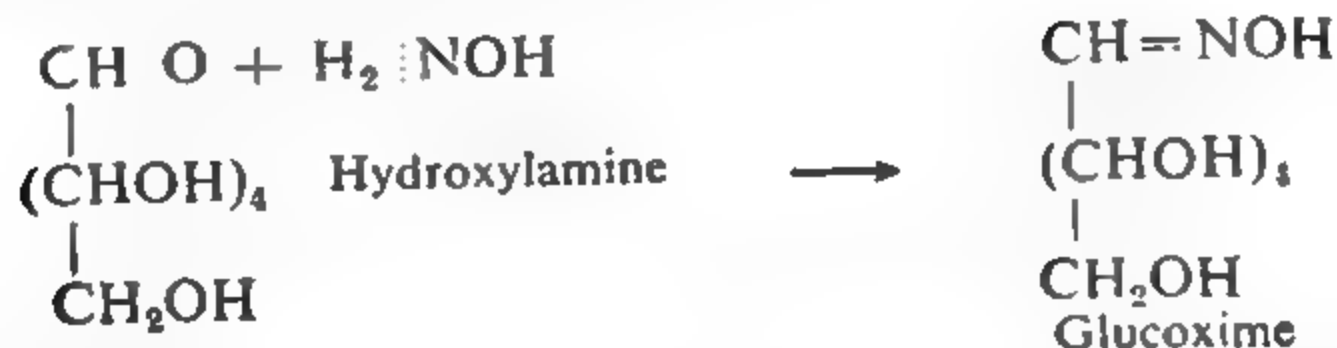


(iv) **Reactions with hydrogen cyanide.** With hydrogen cyanide, glucose gives an addition product, glucose cyanohydrin.

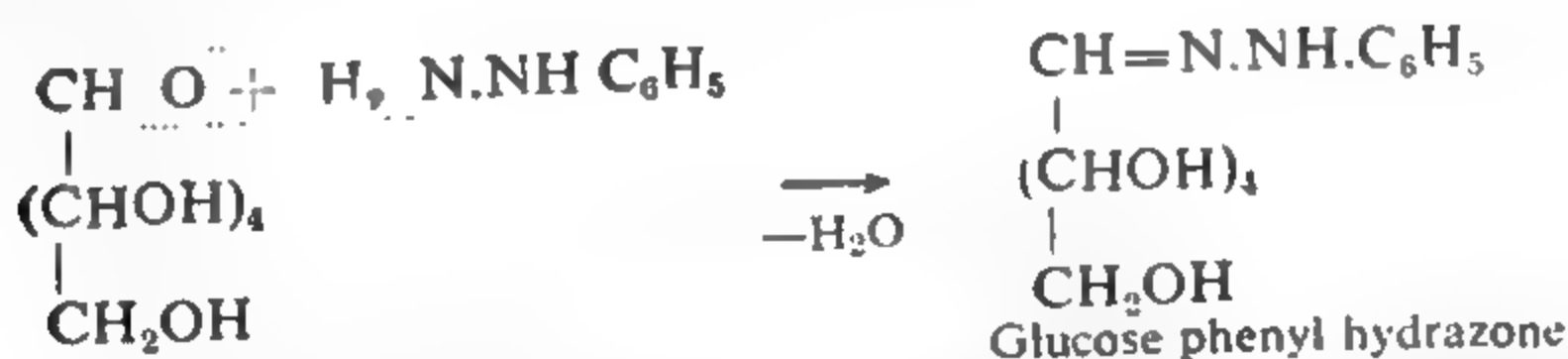
*Fehling solution is prepared by dissolving copper sulphate, NaOH and Rochelle salt (sodium potassium tartrate) in required proportions.



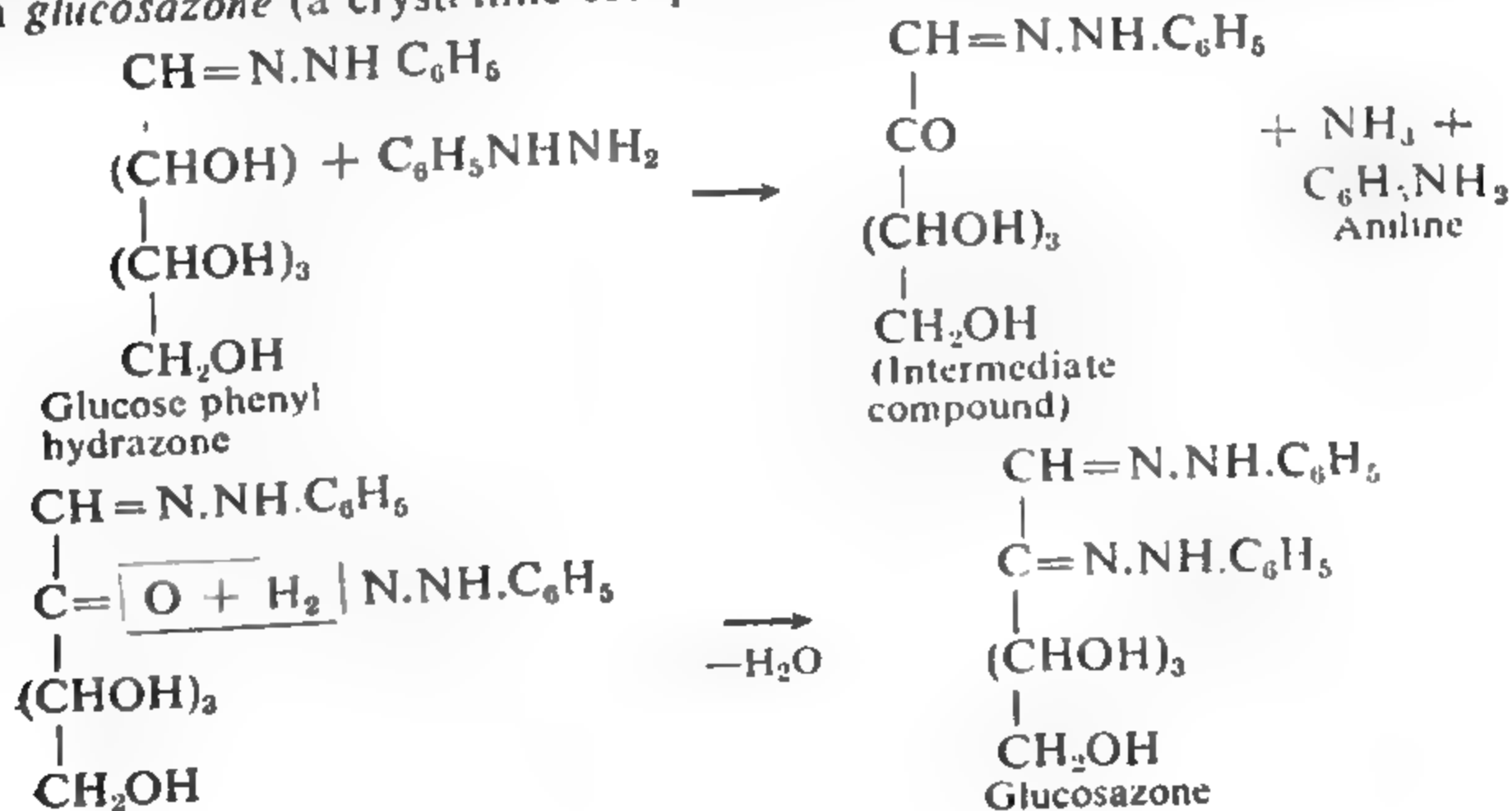
(v) **Reaction with hydroxylamine.** With hydroxylamine, the corresponding *oxime* is formed.



(vi) **Reaction with phenylhydrazine.** Glucose reacts with phenylhydrazine (one molecule) in the usual way forming the corresponding phenylhydrazone.



With an excess of phenyl hydrazine (second molecule), glucose reacts in such a way that the secondary alcoholic group, next to the aldehydic group gets oxidised to form a ketonic group. The intermediate compound so formed reacts with a third molecule of phenyl hydrazine to form *glucosazone* (a crystalline compound, m.p. 205°).



The formation of glucosazone is used as a test for the presence of glucose.

It may be noted that glucose does not react with characteristic aldehydic reagents like sodium bisulphite and ammonia.

(b) Reactions of alcoholic groups.

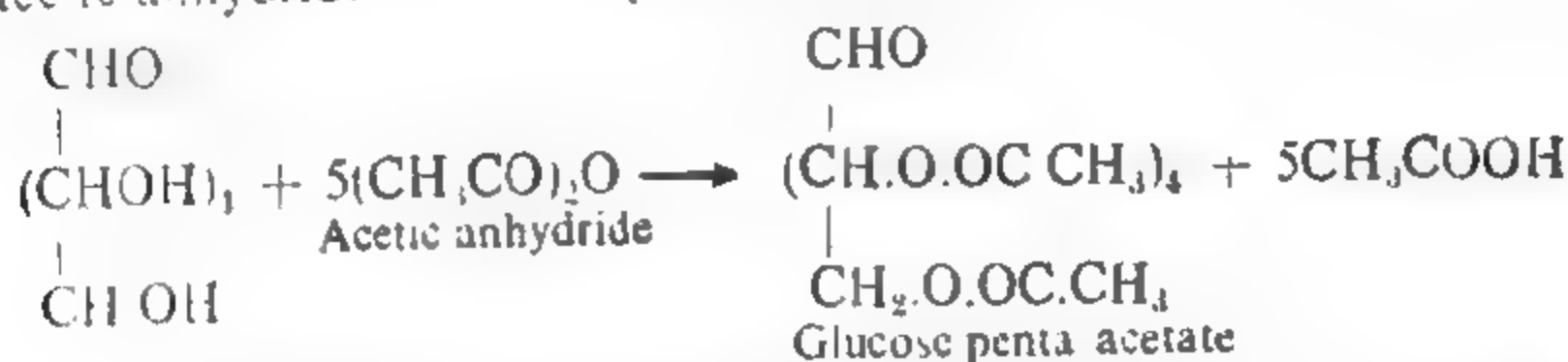
(i) Glucoside formation. Glucose reacts with methyl alcohol, in the presence of dry HCl gas, to form an ether type of compound known as glucoside.



(ii) Glucosate formation. Glucose reacts with calcium hydroxide to form calcium glucosate.



(iii) Acetylation. Glucose reacts with acetyl chloride as well as with acetic anhydride to form a penta-acetyl derivative.



(c) Fermentation. Glucose undergoes fermentation in the presence of yeast to give ethyl alcohol.



Uses. Glucose is used : (i) in preservation of fruits and jams; (ii) in silvering of mirrors; (iii) for synthesising vitamin C and other pharmaceuticals; (iv) in the preparation of wines, vinegars, etc. (v) as a food for invalids.

Tests for Glucose. (i) When warmed with concentrated sulphuric acid, glucose gets charred forming carbon monoxide, carbon dioxide and sulphur dioxide.

(ii) When boiled with a 10% sodium hydroxide solution, it turns yellow.

(iii) When warmed for a few minutes with ammoniacal silver nitrate solution, a shining mirror is formed.

(iv) Glucose when warmed with Fehling solution, forms a red precipitate of cuprous oxide.

(v) With phenyl hydrazine (excess) it gives glucosazone, a yellow crystalline compound (m.p. 202°).

(vi) Molisch's test. This delicate test is given by all carbohydrates and is performed as follows :

Add a few drops of an alcoholic solution of α -naphthol to a solution of glucose

and shake well. Add gently about 2 c.c. of concentrated sulphuric acid along the side of the test-tube. A deep violet coloration develops at the junction of the two layers.

Structure of Glucose. (1) By quantitative analysis, the molecular formula of glucose is found to be $C_6H_{12}O_6$.

(2) Glucose forms a penta-acetyl derivative with acetyl chloride or acetic anhydride indicating the presence of five hydroxyl groups in glucose molecule.

(3) (i) Glucose on mild oxidation with bromine water gives an acid containing the same number of carbon atoms.

(ii) Glucose on reduction gives a primary alcohol, viz., sorbitol.

(iii) Glucose reacts with hydrocyanic acid, hydroxylamine and phenyl hydrazine (1 molecule) to give the corresponding cyanohydrin, oxime and phenylhydrazone respectively.

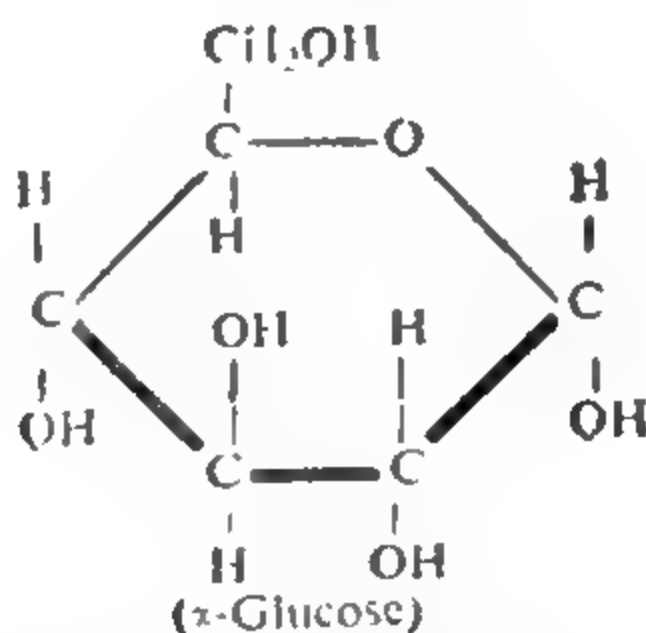
These reactions indicate the presence of aldehydic group in glucose.

Glucose may, thus, be represented as $C_5H_6(OH)_5CHO$.

(4) Glucose is a stable compound. Hence, all the five hydroxyl groups must be attached to different carbon atoms. Glucose may, therefore, be represented as.



It may be pointed out that the above straight chain structure of glucose is not entirely satisfactory, for example, it fails to explain why glucose does not react with sodium bisulphite or ammonia. Earlier work of Tollens, Emil Fischer and more recently that of Haworth has proved that glucose has a cyclic or ring structure, represented below :

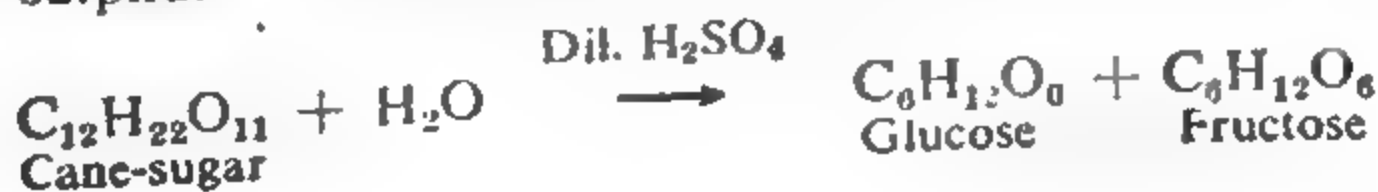


The detailed discussion of the above is beyond the scope of the present volume.

FRUCTOSE, FRUIT SUGAR, LAEVULOSE, $C_6H_{12}O_6$

Fructose occurs in honey and sweet fruits. Cane-sugar on hydrolysis yields equal amounts of glucose and fructose. *Inulin*, a polysaccharide found in *dahlia tubers*, yields only fructose on hydrolysis.

Preparation. (1) Fructose can be obtained *in the laboratory* by the hydrolysis of cane-sugar. For that purpose, cane-sugar is boiled with dilute sulphuric acid till the hydrolysis is complete.

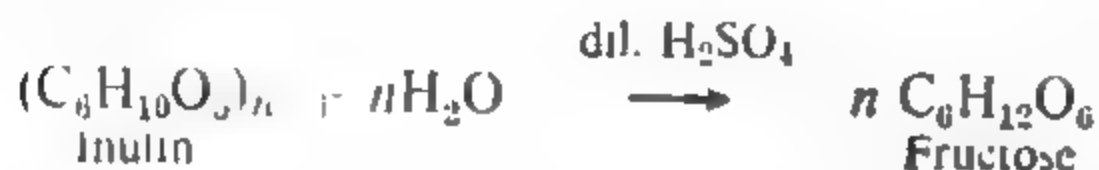


The excess of the acid is neutralised with barium carbonate, and the precipitated barium sulphate is filtered off. The filtrate is then treated with calcium hydroxide when the insoluble calcium fructosate ($\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{CaO}$) gets precipitated (calcium glucosate, being more soluble, remains in solution). The precipitate is separated, suspended in water and a slow current of carbon dioxide is passed which decomposes the fructosate.



The insoluble calcium carbonate is filtered off, and the filtrate concentrated to yield crystals of fructose.

(2) On an industrial scale, fructose is obtained by the hydrolysis of inulin, present in *dahlia tubers* and *jerusalem artichoks*, with dilute sulphuric acid.



After completion of the hydrolysis, which takes nearly an hour, the excess of the acid is neutralised by baryta (BaO). The filtrate, on concentration under reduced pressure, yields crystals of fructose as a hemihydrate $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$.

Physical Properties. Fructose is a colourless crystalline solid (m.p. 95°). It is soluble in water and alcohol.

Chemical Properties. Fructose has the structure,

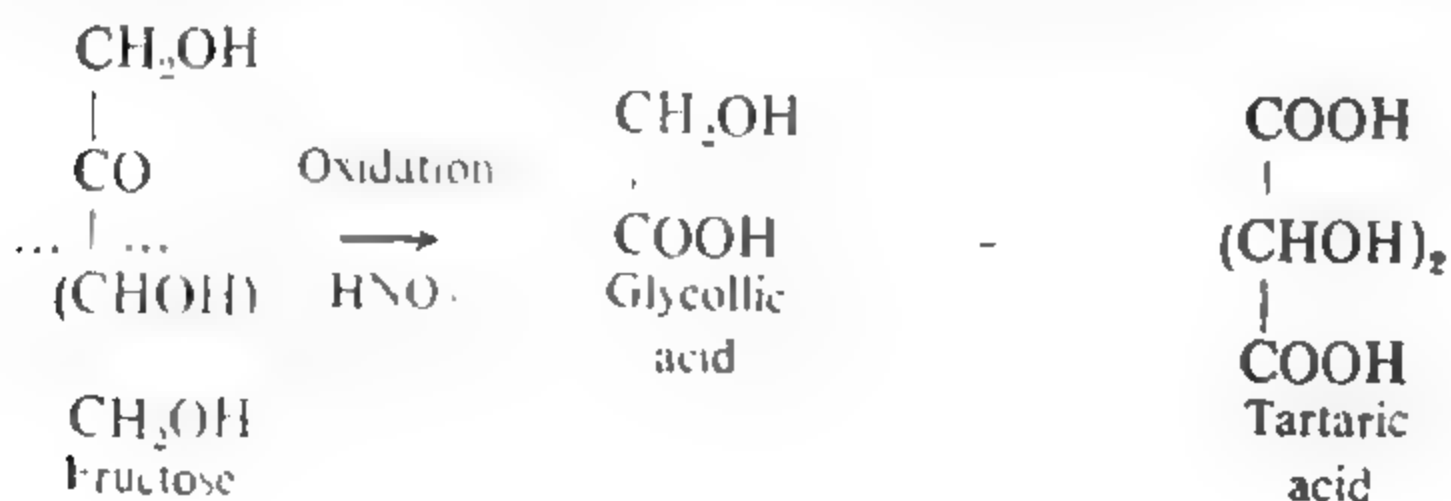


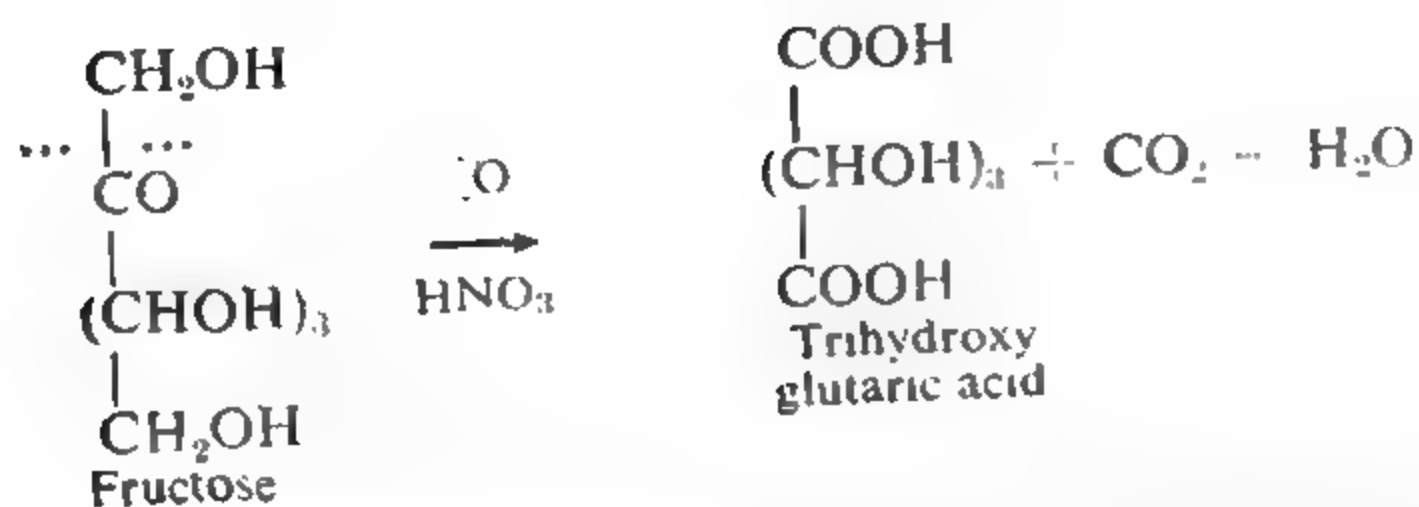
It contains one ketonic and five hydroxyl groups. Fructose, therefore, combines the properties of a ketone and a polyhydric alcohol.

(a) **Reactions of the ketonic group.**

(1) **Oxidation.** Mild oxidising agents like bromine water have no action on fructose.

Strong oxidising agents like nitric acid oxidise fructose to give a mixture of three acids—trihydroxy glutaric, tartaric and glycollic acids, each containing fewer number of carbon atoms than fructose.



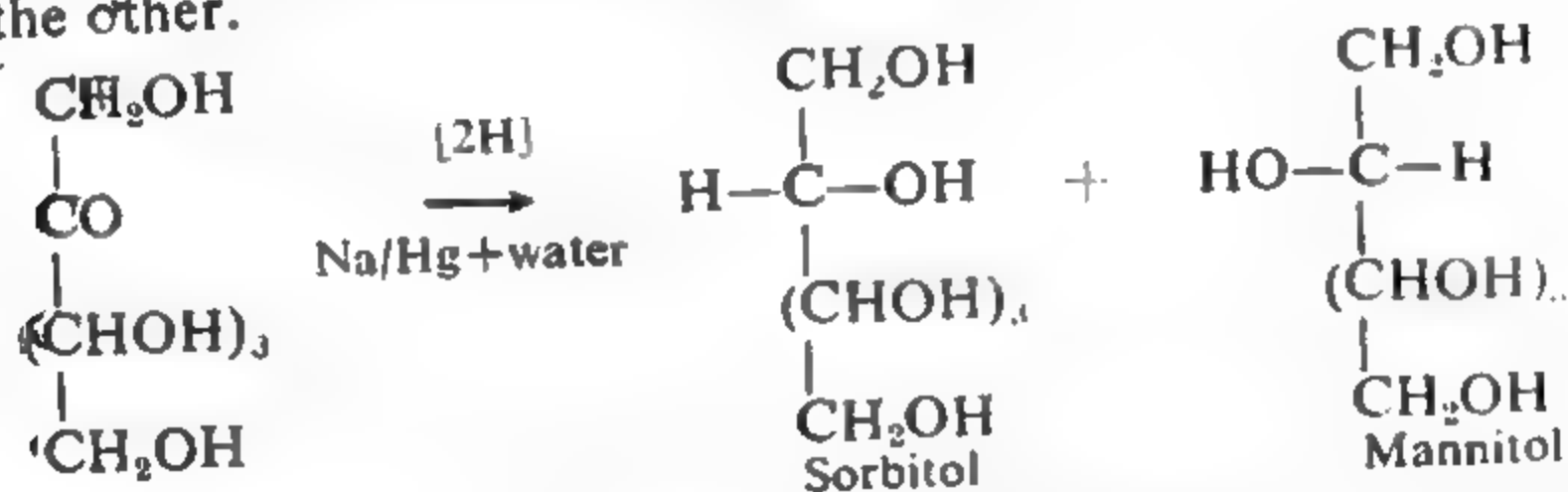


(2) **Reducing properties.** Since fructose, like glucose, can be easily oxidised, it behaves as a reducing agent.

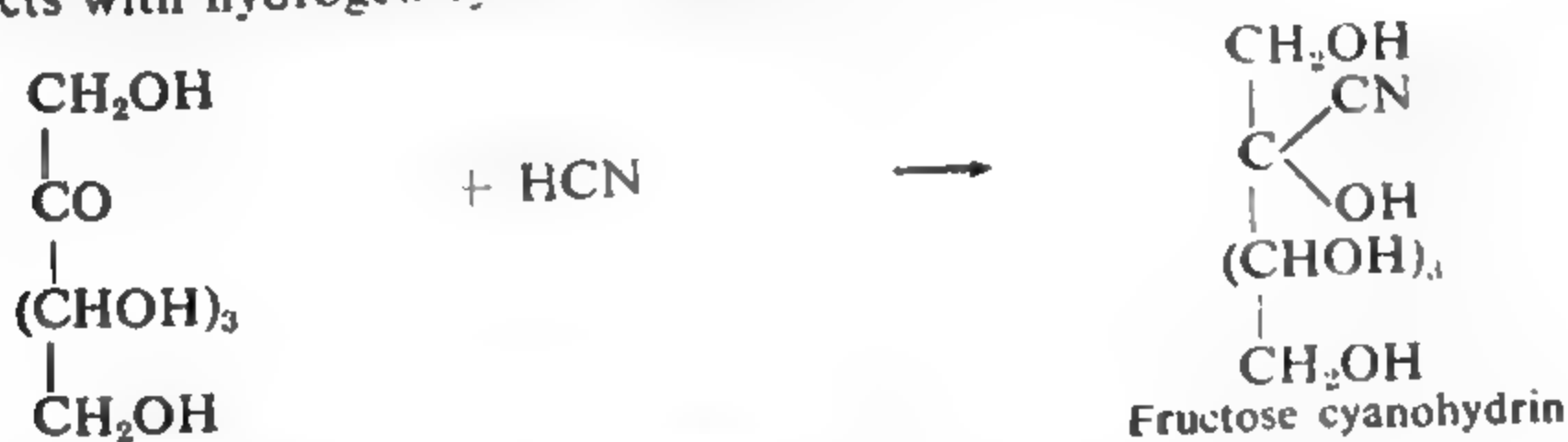
It reduces ammoniacal solution of silver nitrate to metallic silver and Fehling solution to red cuprous oxide.

The reducing action of fructose is due to the presence of $-\text{CO} \cdot \text{CH}_2\text{OH}$ group in it.

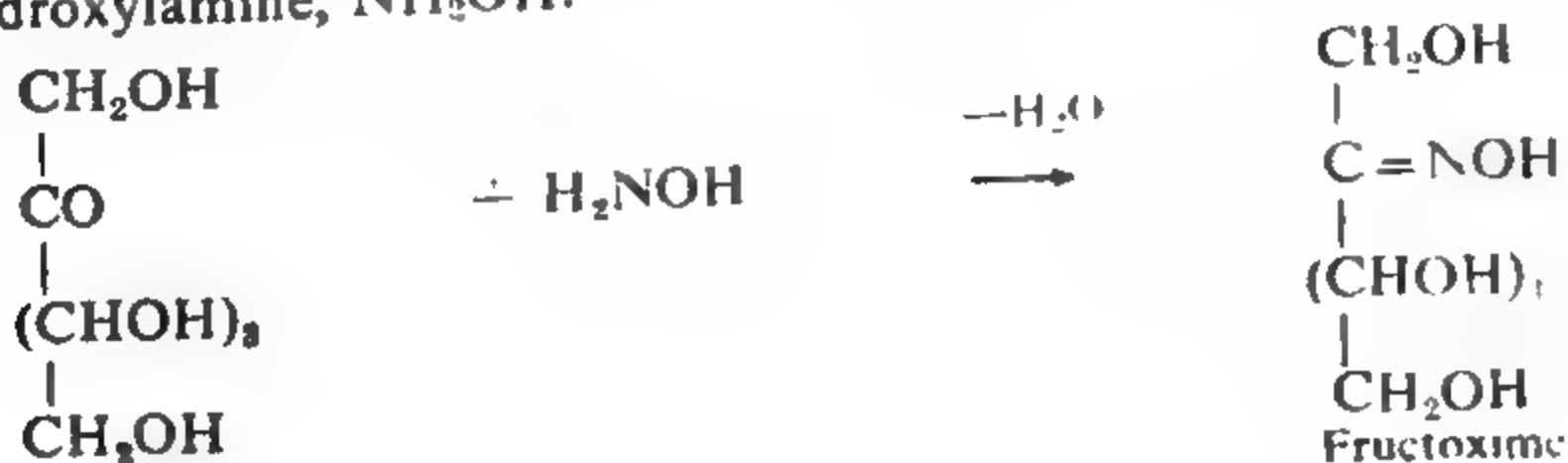
(3) **Reduction.** With sodium amalgam and water, fructose gives a mixture of alcohols—sorbitol and mannitol, each being an optical isomer of the other.



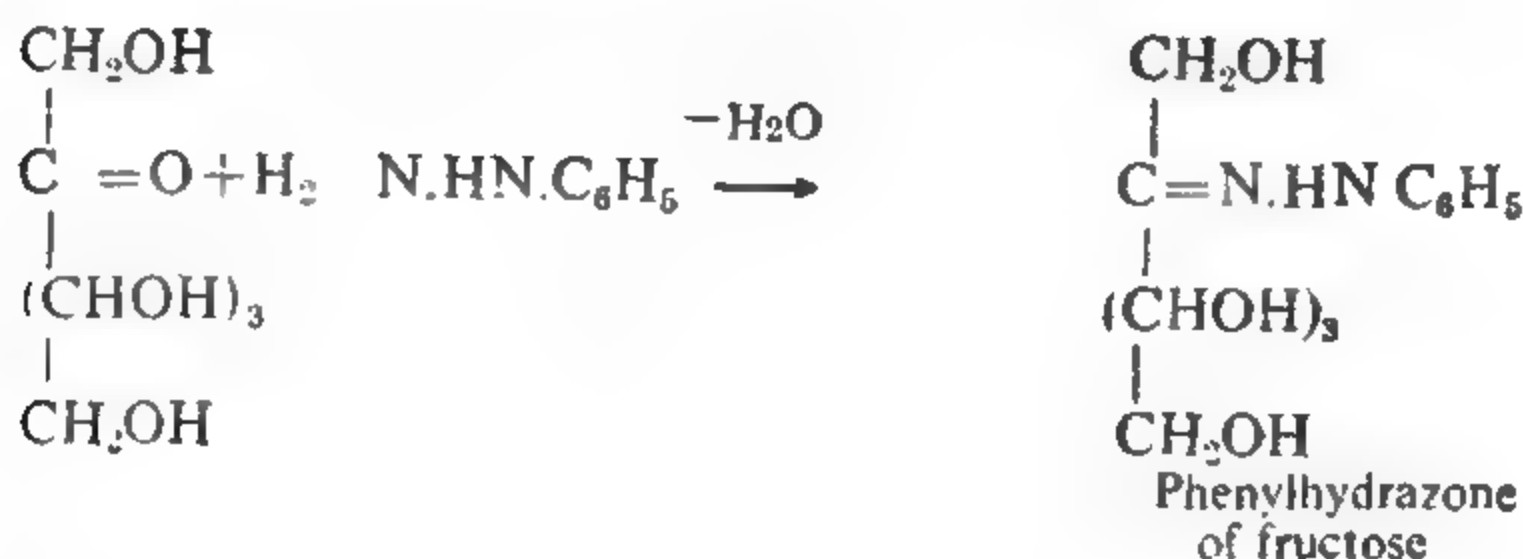
(4) **Reaction with hydrogen cyanide.** Fructose, like other ketones, reacts with hydrogen cyanide to form a cyanohydrin.



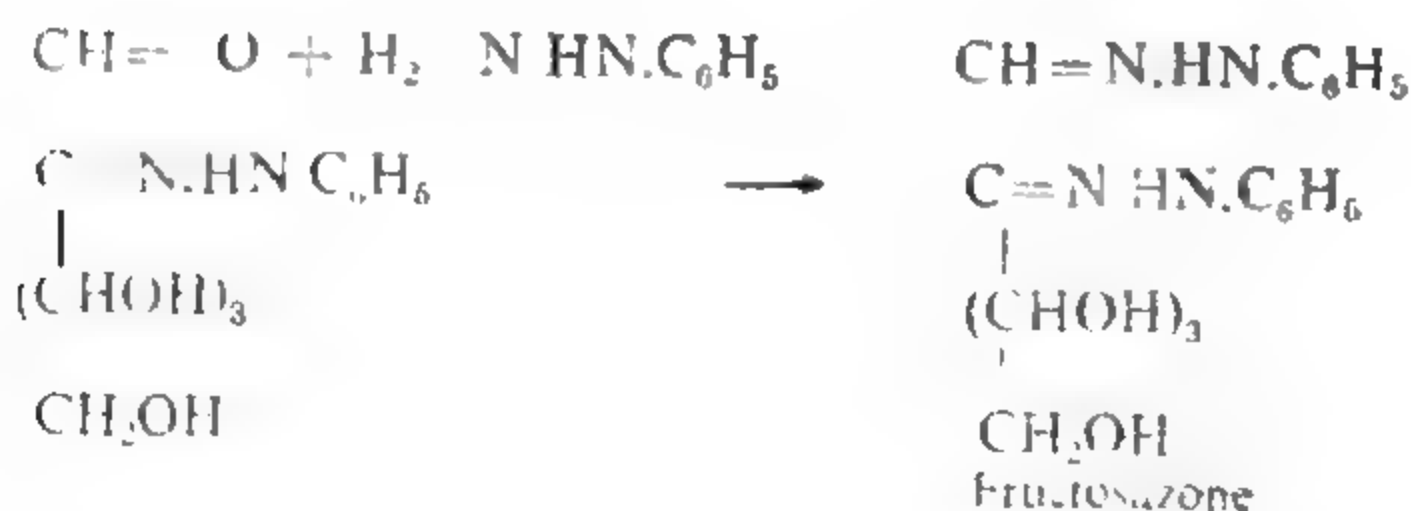
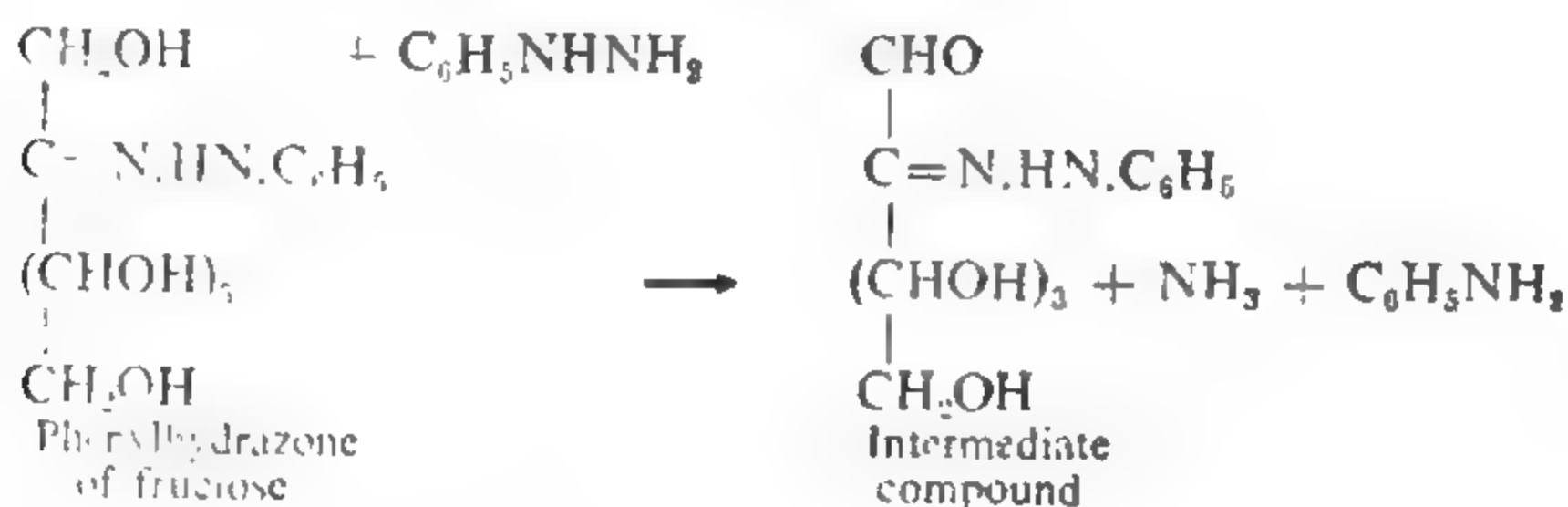
(5) **Reaction with hydroxylamine.** Fructose forms an oxime with hydroxylamine, NH_2OH .



(6) **Reaction with phenylhydrazine.** Fructose reacts with phenylhydrazine (1 molecule) to form the corresponding phenylhydrazone.



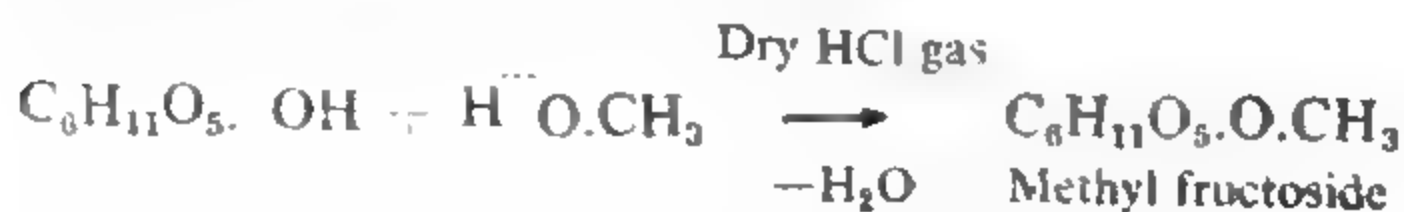
The phenylhydrazone so formed reacts with excess of phenyl hydrazine (second molecule) in such a way that the primary alcoholic group present at the end, adjacent to ketonic group, gets oxidised to the aldehydic group. This intermediate compound reacts with another molecule of phenylhydrazine to form an *osazone*, fructosazone.



It may be of interest to note that the fructosazone formed is found to be identical with glucosazone (both melt at 205°).

(b) **Reactions of the alcoholic groups.**

(1) **Fructoside formation.** Fructose forms a fructoside with methyl alcohol in the same manner as glucose does.

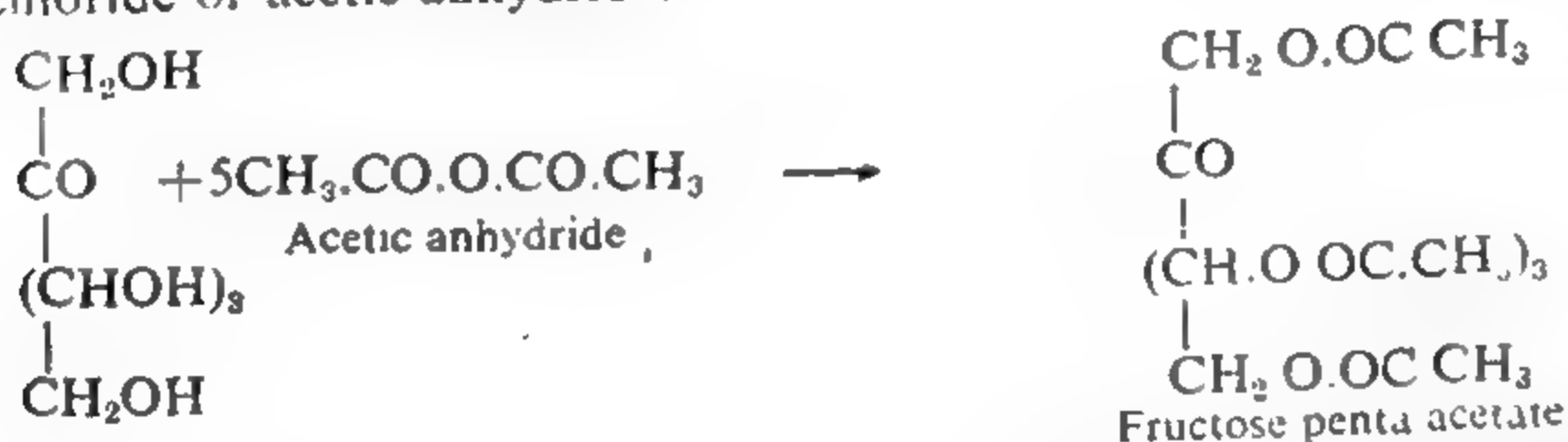


Methyl fructoside, like methyl glucoside, is also an ether type of compound.

(2) **Fructosate formation.** Fructose reacts with hydroxides of calcium, barium or strontium to form the corresponding fructosates.



(3) **Acetylation.** Fructose forms penta-acetyl derivative with acetyl chloride or acetic anhydride.



(c) **Fermentation.** Fructose, like glucose, undergoes fermentation in the presence of yeast, forming ethyl alcohol and carbon dioxide.



Uses. Fructose is used as a sweetening agent in place of cane-sugar.

Tests for Fructose. Fructose gives all the tests mentioned under glucose except number 2.

In addition, the following tests are also given :

(1) *Selivanoff's test* If a little of fructose is warmed with some resorcinol in dilute hydrochloric acid, a red coloration or precipitate is formed.

(2) *Pinoff's test.* When a little of fructose is warmed with a little of ammonium molybdate solution containing a few drops of glacial acetic acid, a deep blue coloration is developed.

Structure of Fructose

(1) From preliminary analysis, empirical formula of fructose comes out to be CH_2O . Its molecular weight being 180, the molecular formula is $(\text{CH}_2\text{O})_6$ or $\text{C}_6\text{H}_{12}\text{O}_6$.

(2) Its reaction with acetyl chloride, forming a penta-acetyl derivative, indicates the presence of five hydroxyl ($-\text{OH}$) groups.

(3) Its reaction with hydrocyanic acid, hydroxylamine and phenyl hydrazine (1 molecule only) forming cyanohydrin, oxime, and phenyl hydrazone respectively, shows the presence of an aldehydic group or a ketonic group.

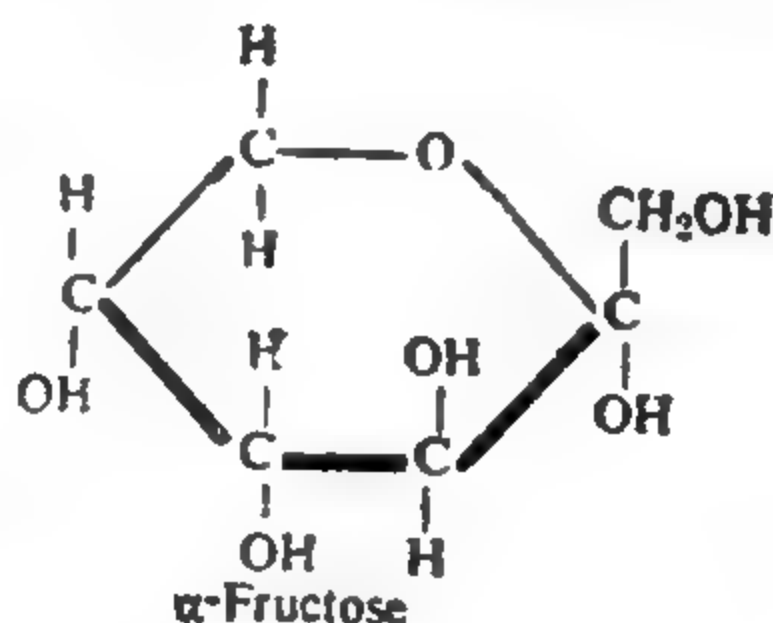
(4) That there is a ketonic group and not an aldehydic group is established by the following :

(a) Reduction gives not one, but a mixture of two alcohols, viz., sorbitol and mannitol.

(b) Mild oxidation has no effect on fructose. Strong oxidation produces a mixture of acids (tartaric, glycolic and trihydroxy glutaric) each of which contains a fewer number of carbon atoms. Therefore, fructose can be represented as :



As in the case of glucose, the straight chain structure of fructose is inadequate for various reasons which cannot be discussed in the present volume. Suffice it to say that considerations, very similar to those applicable for glucose, have led to the conclusion that fructose has a closed ring structure, viz.,



Interconversions of Glucose and Fructose

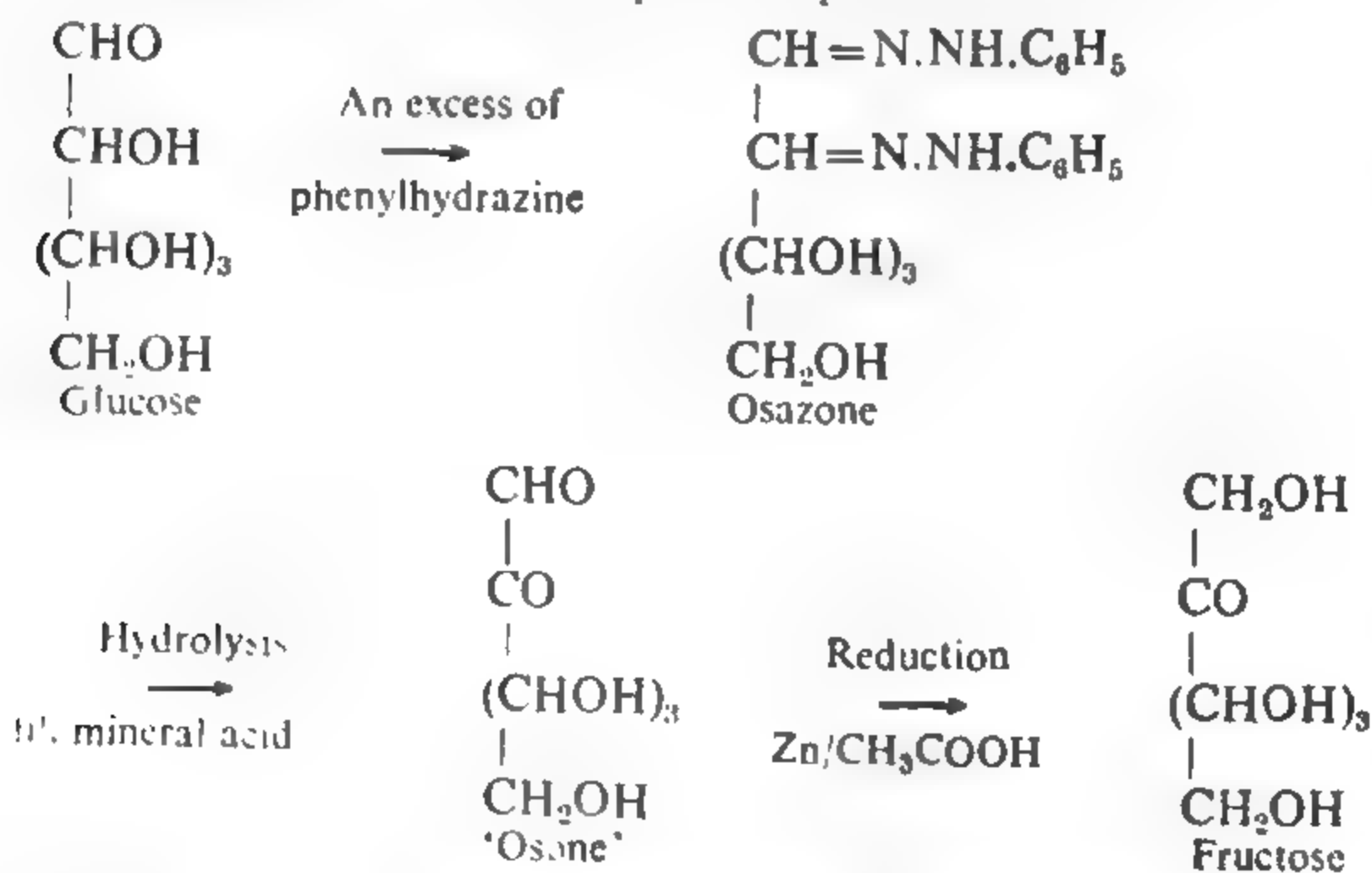
(a) **Conversion of Glucose into Fructose.** This is brought about in the following steps :

(i) Glucose is reacted with an excess of phenylhydrazine, when glucosazone is formed.

(ii) The glucosazone on hydrolysis with a dilute mineral acid yields a keto-aldehyde, called 'osone'.

(iii) This keto-aldehyde, or *osone*, on reduction with zinc dust and acetic acid is converted into fructose because the aldehydic group is reduced in preference to the keto group.

Schematically, the above steps are represented below :



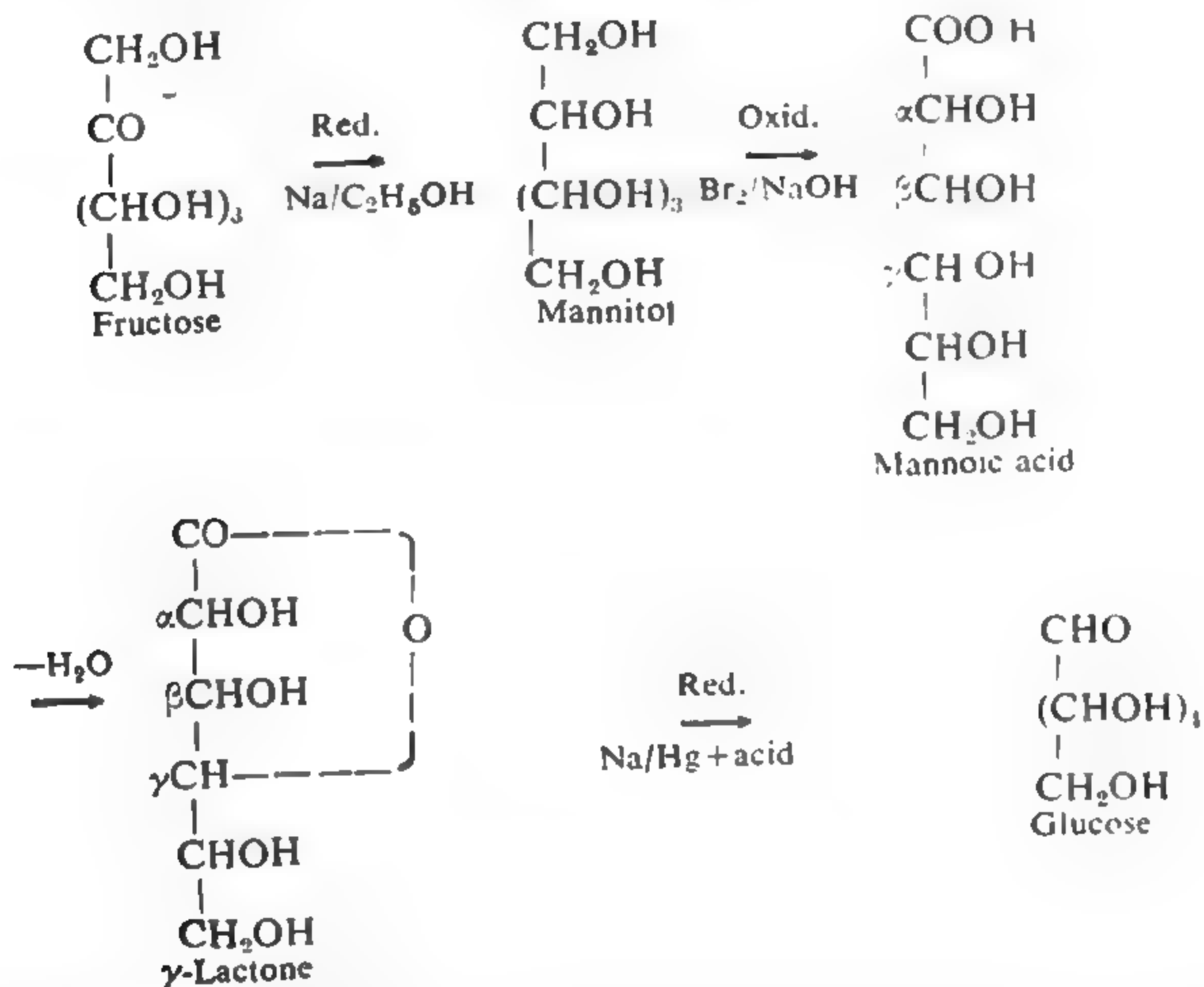
b **Conversion of fructose into glucose.** This is effected in the following steps

(i) Fructose is reduced with Na C₂H₅OH when a mixture of sorbitol and mannitol is obtained.

(ii) Mannitol on mild oxidation with bromine water in the presence of alkali yields a mono-carboxylic acid which immediately is converted into γ -lactone (inner hydride of a γ -hydroxy acid).

(iii) The γ -lactone is then reduced with sodium amalgam and dilute sulphuric acid, when glucose is obtained.

The above steps may be represented as below :



Comparison of Glucose and Fructose. The detailed study of glucose and fructose has proved conclusively that while glucose is an aldohexose, fructose is a keto-hexose.

A comparison of their properties is summed up as below :

Common Properties :

1. Both are crystalline, sweet in taste, soluble in water.
2. Both react with HCN, NH_2OH and phenyl hydrazine. With excess of phenyl hydrazine, both give the same compound, glucosazone.
3. Both reduce ammoniacal solution of silver nitrate and Fehling solution.
4. Both react with acetyl chloride or acetic anhydride giving a penta-acetyl derivative.
5. Both react with methyl alcohol forming ether-like compounds.
6. Both react with calcium hydroxide.

Different Properties :

1. Glucose is dextro rotatory while fructose is laevo rotatory.
2. Glucose on reduction gives only one alcohol, sorbitol, whereas fructose yields a mixture of two alcohols, sorbitol and mannitol.
3. Glucose is readily oxidised to gluconic acid even with mild oxidising agents, such as bromine water. Fructose is a little resistant towards oxidation. On drastic treatment, however, it gives a mixture of three acids, namely glycollic, tartaric and trihydroxy glutaric acids. Glucose on drastic oxidation gives only one acid, namely saccharic acid.

Cane-sugar, Beet-sugar, Sucrose $C_{12}H_{22}O_{11}$

Cane-sugar is one of the most commonly used carbohydrates. It is known to mankind from very early times and has been used as a sweetening agent. It is present in sugar-cane and in beet in appreciable proportions and is also present in small amounts in fruits like pineapple, banana, strawberries, etc. The commercial sources of cane-sugar are sugar-cane and beets, in both of which the sugar content is about 15-18 per cent. Chemically, both the cane-sugar and beet sugar are identical.

Manufacture. The manufacture of cane-sugar or sucrose is carried out in the following steps :

(i) **Extraction of juice.** The freshly cut sugar-cane is crushed and pressed by passing through a set of rollers when the juice is squeezed out. In order to extract the juice completely, hot or cold water is sprayed on the fibrous material when it is on its way to the set of rollers. This ensures almost complete extraction of juice. The residue of the fibrous material, industrially known as *bagasse*, is used either as a fuel for the boilers or for manufacturing *celotex* (a type of insulating board).

The juice falls down in a drain and is carried into a tank.

For the extraction of juice from the beets, the latter are washed, cut into thin slices and treated with water at about 80–90°, when the sucrose gets extracted by the process of dialysis*. The pulp (corresponding to *bagasse* in the above process) is a valuable food. The juice obtained by either of the processes is sent to another tank for **clarification**.

(ii) **Clarification of the juice.** The raw juice is a brownish liquid containing about 15–18% of sucrose along with small amounts of other substances such as organic acids, colouring matter, nitrogenous compounds (proteins), mineral salts and some suspended *bagasse* particles. The juice is purified by (a) *defecation* (b) *carbonation* and (c) *sulphitation*.

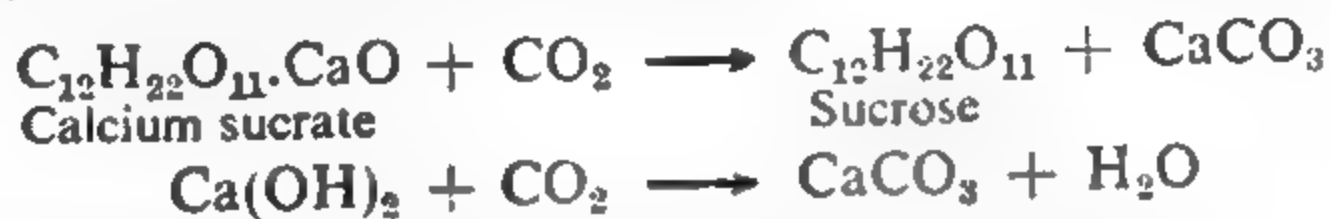
(a) **Defecation.** The raw juice, soon after its extraction, is transferred into a tank heated with steam coils, and treated with 2–3 per cent lime (*defecation*), till the solution is just alkaline. The organic acids are converted into their calcium salts which are precipitated. Some sucrose also reacts with lime forming calcium sucrate.



*Dialysis is a process wherein crystalloids are separated from the colloids by means of a semipermeable membrane.

But since it is soluble, it remains in solution. The proteinous matter gets coagulated and forms a scum at the top along with other suspended impurities. On passing through a filter press, both the scum and the precipitated impurities are removed.

(b) **Carbonation.** The filtrate containing a slight excess of lime and soluble calcium sucate ($C_{12}H_{22}O_{11} \cdot CaO$) is transferred into another tank and carbon dioxide is bubbled through it (*carbonation*). Carbon dioxide decomposes the calcium sucate to yield sucrose and calcium carbonate, and also reacts with unreacted lime.



The precipitated calcium carbonate is filtered off.

(c) **Sulphitation.** The juice is now treated with sulphur dioxide (*sulphitation*) which serves a dual purpose. Firstly, it decomposes any undecomposed calcium sucate and also removes any residual lime as calcium sulphite. Secondly, it bleaches the sugar solution. The precipitated calcium sulphite is removed by filtration. For better results, operations (b) and (c) may be repeated.

(iii) **Concentration and Crystallisation.** The clarified juice is concentrated under reduced pressure in 'multiple effect' evaporators. (Fig. 1).

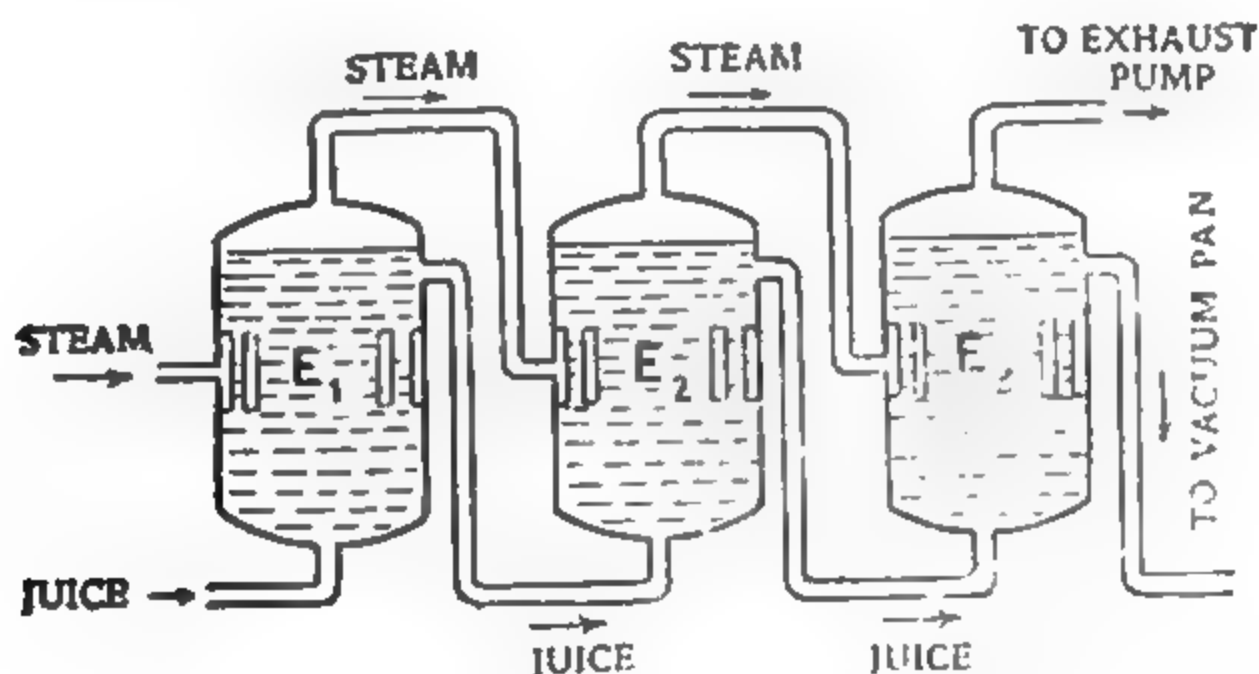


Fig. 1. Multiple Effect Evaporators

This device, resorted to in order to economise fuel, will be clear from the following description. Exhaust steam from the engine is admitted into the first evaporator, E_1 , where a pressure P_1 (below normal) is maintained. The liquid in evaporator E_1 boils and steam from E_1 is used for boiling liquid in evaporator E_2 under pressure P_2 (less than P_1) and steam from E_2 is used for boiling liquid in evaporator E_3 under a still lesser pressure P_3 . The liquids in evaporators E_1 and E_2 are the concentrates from evaporators E_1 and E_2 respectively.

When sufficient concentration has been observed, the concentrate is taken into a vacuum pan and further concentrated till crystals appear. The contents (*massacuite*), at this stage, are transferred into a crystallisation tank and allowed to crystallise.

(iv) **Separation and drying of crystals.** The crystals along with the mother liquor (*molasses*) are taken in a centrifugal machine. On operating the machine, the mother liquor is drained away and sugar crystals are obtained which have a slightly brownish colour due to the sticking molasses. Cold water is sprayed over the crystals and again centrifuged*. The wet crystals so obtained are dropped from the top of a tall chimney, from the bottom of which hot air goes up. The crystals falling down get completely dried and are collected in bags. A flow sheet for the manufacture of cane-sugar is shown in Fig. 2.

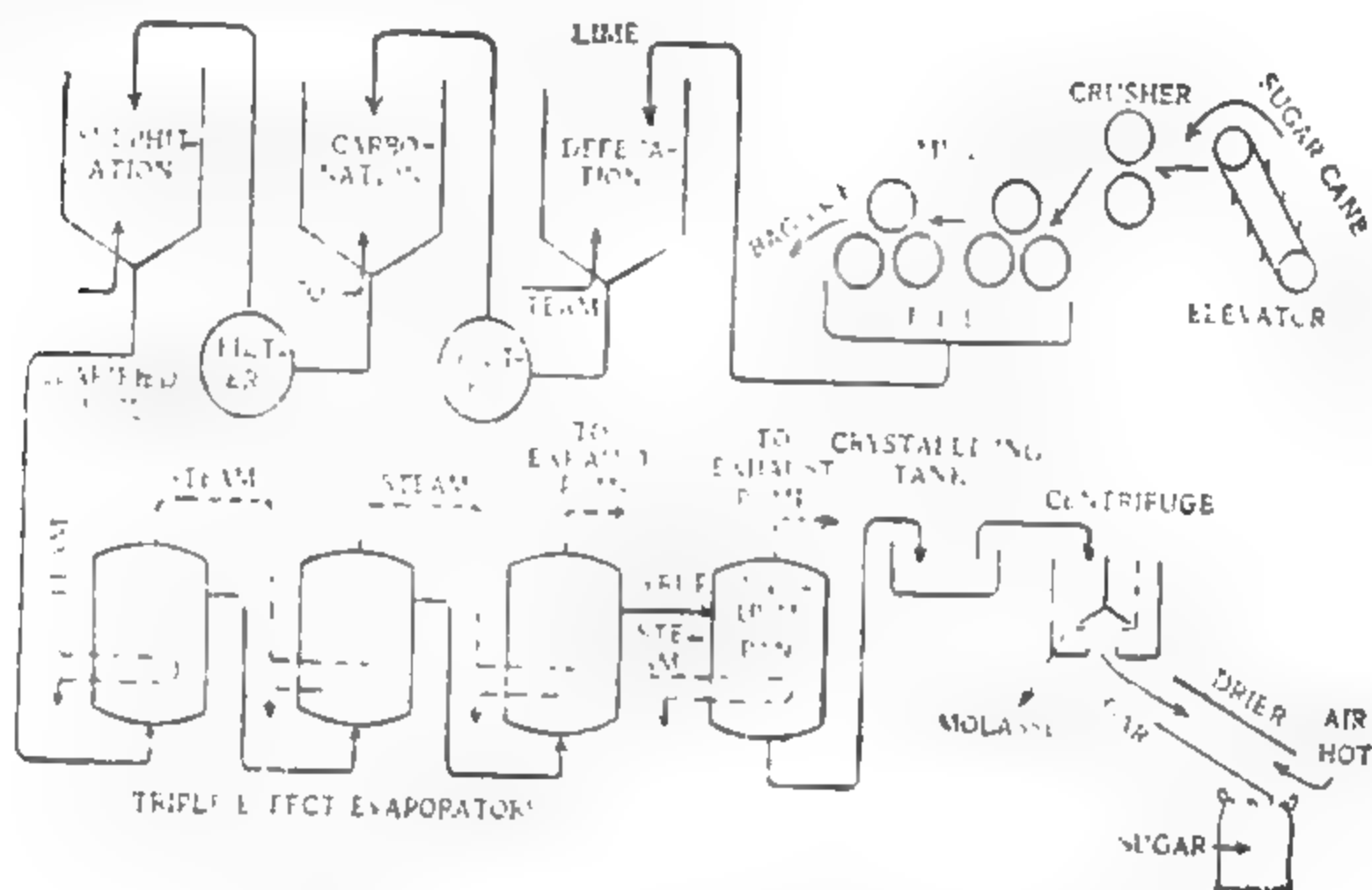


Fig. 2. Flow sheet for manufacture of Cane-sugar

The mother liquor (molasses) still contains about 50% of sugar. Quite often a second crop of cane-sugar is obtained from it through formation of strontium sucate followed by its decomposition with carbon-dioxide. Molasses is a very suitable and cheap source of manufacturing alcohol.

Physical Properties (1) Cane-sugar is a white crystalline solid (m.p. 184°) soluble in water, but insoluble in alcohol.

(2) Its aqueous solution is optically active and is dextro-rotatory, specific rotation being $+66.5^\circ$.

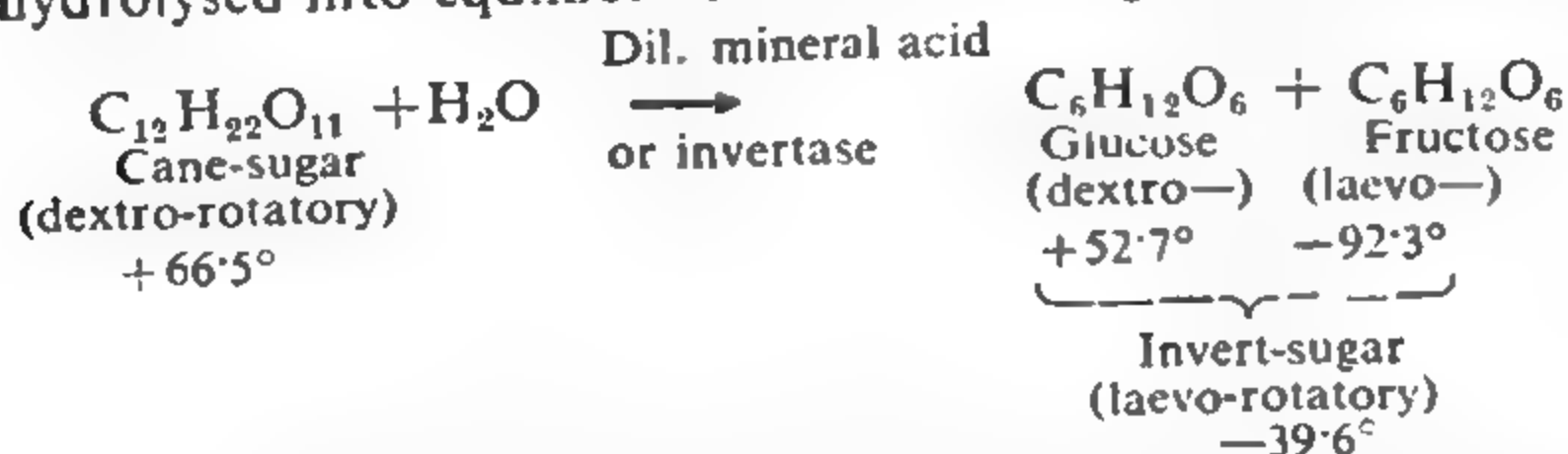
(3) When heated to a temperature just above its melting point and allowed to cool, it solidifies to give an amorphous glassy mass called *barley sugar*, which, if allowed to stand for some time, transforms back into the crystalline form.

(4) On heating to 200°, it loses some water and gives a brownish mass, called *caramel*, which is commonly used as a flavouring and colouring material for confectionery and wines.

(5) On heating still further, cane-sugar gets charred and gives sugar-charcoal.

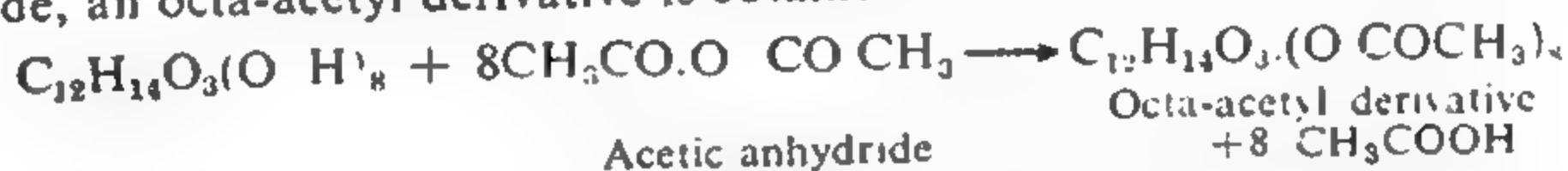
*Very often some ultramarine is mixed with water, which imparts a white colour to sugar crystals.

Chemical Properties. (1) **Hydrolysis.** On treatment with dilute mineral acids or by the action of an enzyme, *invertase*, cane-sugar is hydrolysed into equimolecular mixture of glucose and fructose.



This equimolecular mixture is known as *invert sugar* because *inversion* of rotation has occurred. This fact would be very easily understood if it is remembered that fructose is more strongly laevorotatory than the dextro-rotatory character of glucose. This phenomenon is called **inversion of cane-sugar**.

(2) **Acetylation.** On treatment with acetic anhydride or acetyl chloride, an octa-acetyl derivative is obtained.



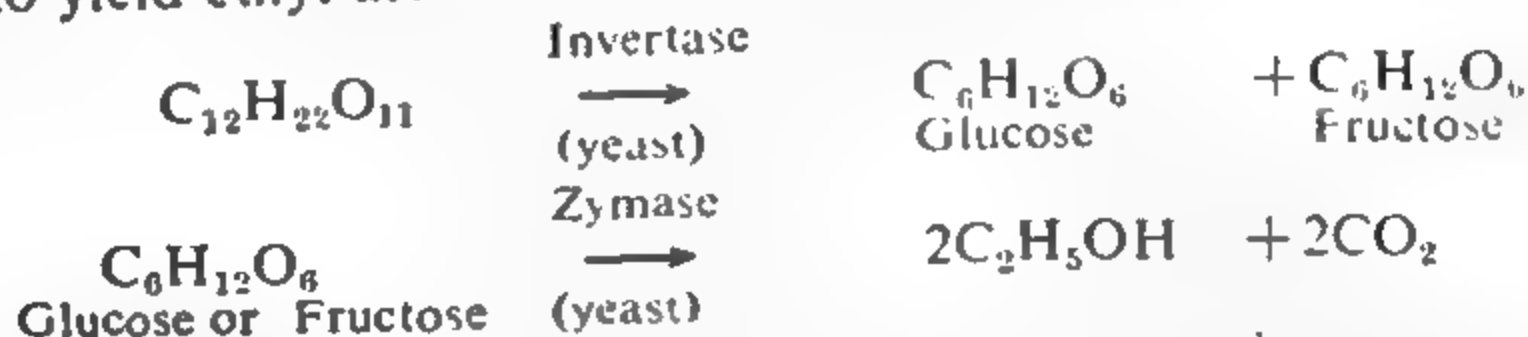
The reaction indicates the presence of eight hydroxyl groups in a molecule of cane sugar.

(3) **Non-reducing character.** Cane-sugar does not reduce Fehling solution or ammoniacal silver nitrate. It also does not react with hydrocyanic acid, hydroxylamine or phenyl hydrazine. All this leads to the conclusion that no carbonyl group, $>\text{C}=\text{O}$, is present in cane-sugar.

(4) **Formation of sucrate.** With calcium hydroxide or strontium hydroxide, calcium or strontium sucrate is formed.

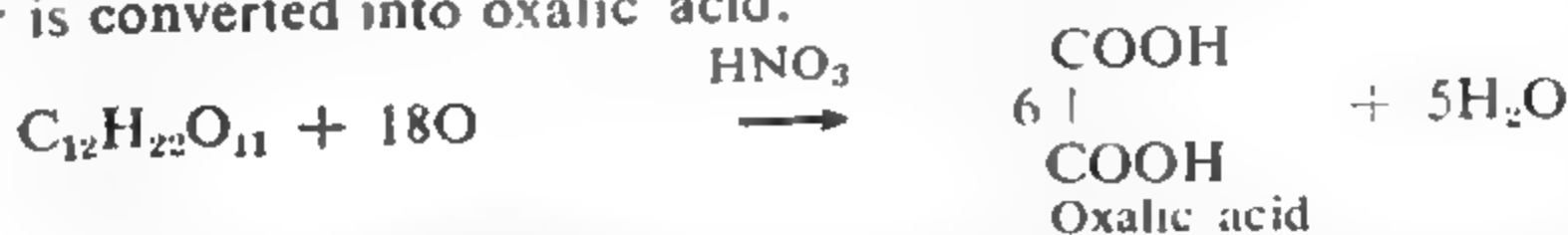


(5) **Fermentation.** In the presence of yeast, sucrose undergoes fermentation to yield ethyl alcohol and carbon dioxide.



Both the enzymes, viz., invertase and zymase are present in yeast.

(6) **Oxidation.** When oxidised with concentrated nitric acid, cane-sugar is converted into oxalic acid.



(7) **Action of concentrated sulphuric acid.** With concentrated sulphuric acid, cane-sugar is charred even in cold with the production of carbon dioxide and carbon.



Uses. Cane-sugar is very widely used as (a) a sweetening agent (b) as a food (c) as a preservative for fruits and (d) in the form of its octa-acetate for denaturing alcohol and for rendering paper transparent.

Tests. (1) Heat a little of sucrose, a brown mass, caramel, is obtained. On further heating, charring occurs with a characteristic smell.

(2) Take a little of sucrose and add conc. H_2SO_4 . Charring is noticed with the evolution of CO_2 and SO_2 .

(3) Boil a small amount of cane-sugar solution with some dil. HCl . Add Fehling solution and warm. A red precipitate of Cu_2O is formed. (why?)

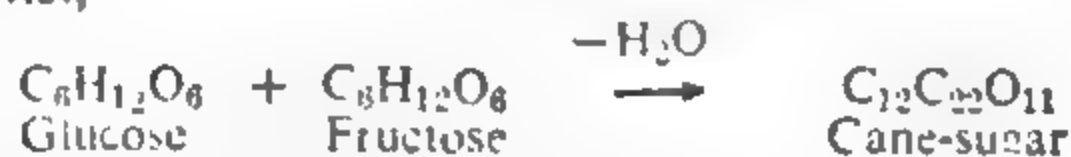
(4) It responds to Molisch's test (see under glucose).

Structure of Sucrose. (1) Preliminary analysis and molecular weight determination indicate that the molecular formula of sucrose is $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.

(2) Sucrose forms an octa-acetyl derivative with acetyl chloride or acetic anhydride. It shows the presence of eight $-\text{OH}$ groups in a cane-sugar molecule.

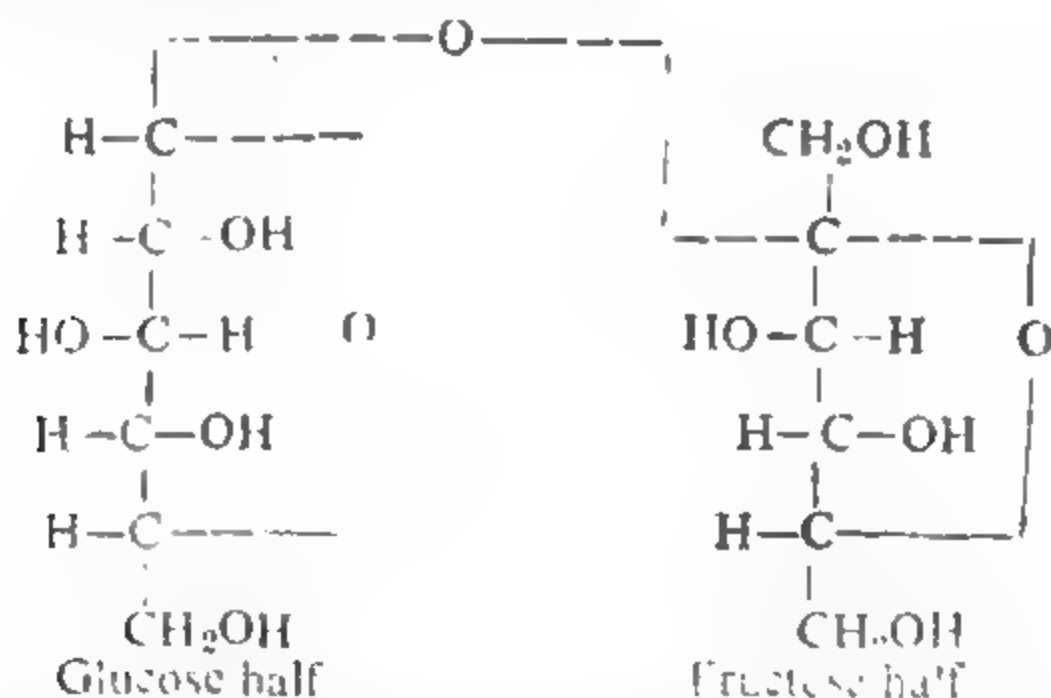
(3) Sucrose does not reduce Fehling solution or ammoniacal silver nitrate. Neither does it react with hydroxylamine, hydrogen cyanide or phenyl hydrazine. This indicates the absence of a $>\text{C}=\text{O}$ group.

(4) On hydrolysis, sucrose yields an equimolecular mixture of glucose and fructose. Thus, it means that a sucrose molecule is theoretically built up by a union of one molecule of each of glucose and fructose through the elimination of a water molecule, viz.,



The linking is such that the aldehydic group in the glucose molecule and the ketonic group in the fructose molecule are masked.

Much work associated with the name of Haworth (1916) has established that cane-sugar has the following structure :

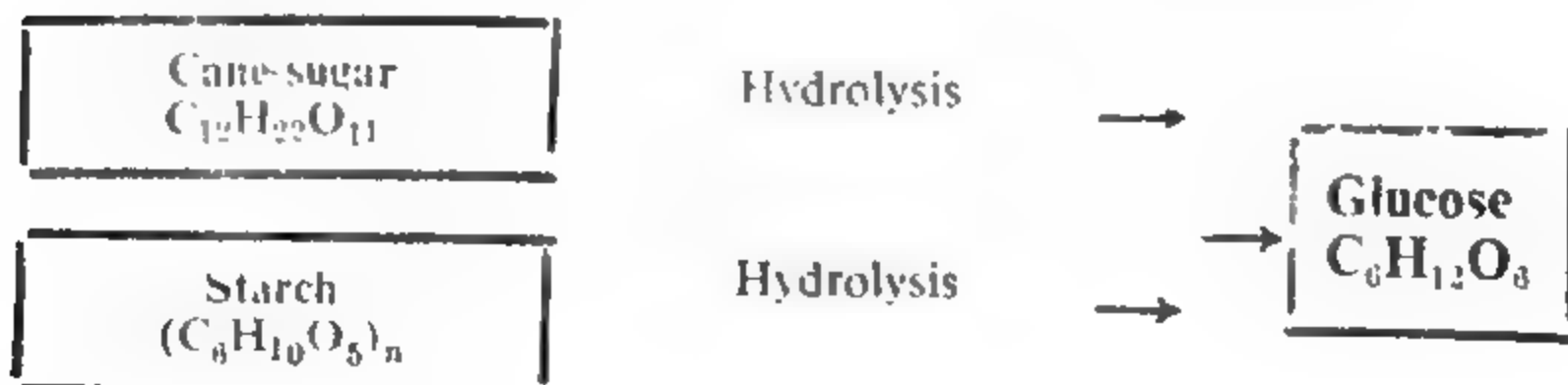


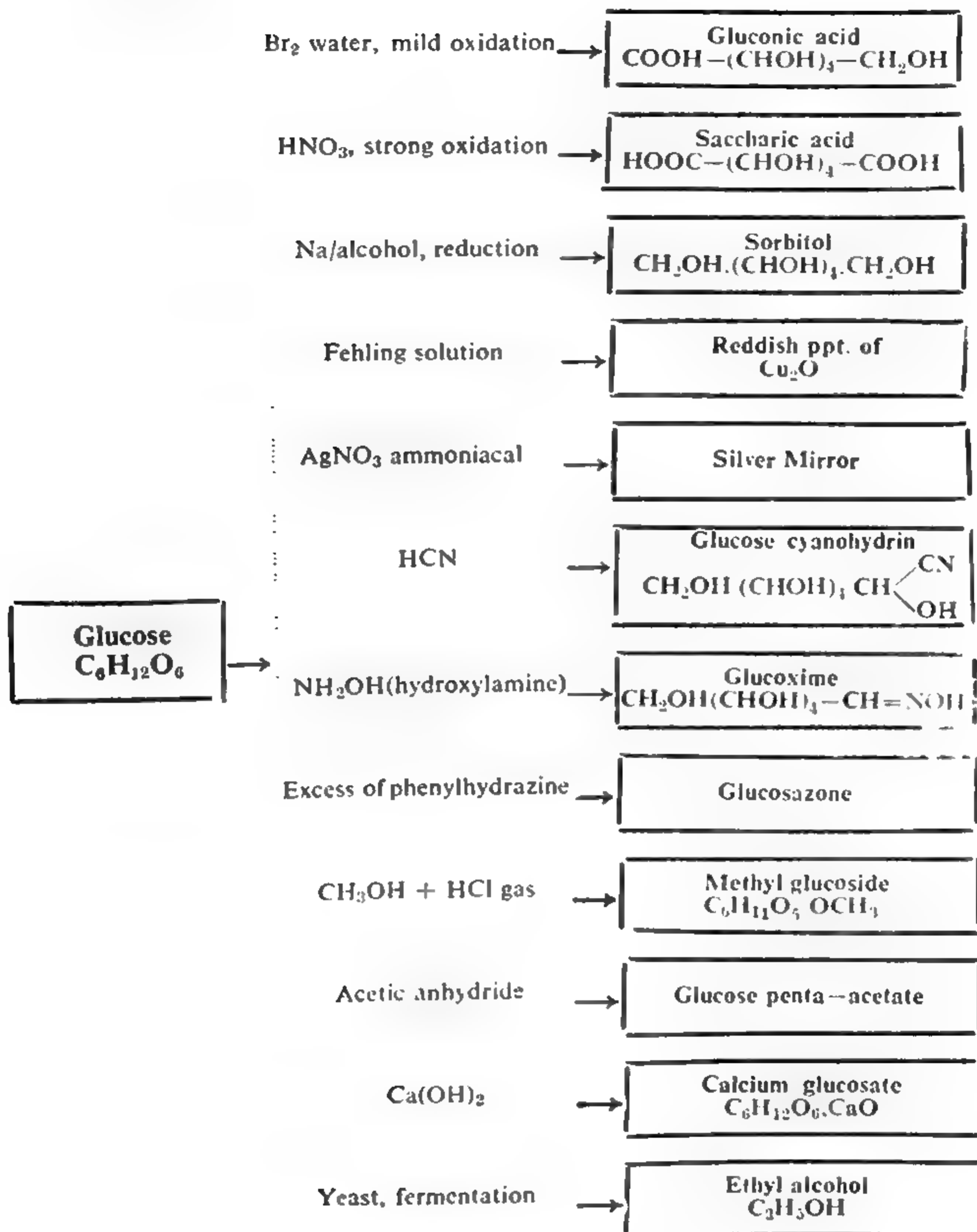
The detailed discussion is beyond the scope of the present book.

SUMMARY OF A TYPICAL MEMBER

PREPARATION AND PROPERTIES OF GLUCOSE

Preparation.



Properties.**QUESTIONS**

1. What are carbohydrates? How have they been classified? Illustrate your answer with suitable examples.

2. How is glucose prepared (a) in laboratory (b) on an industrial scale ?

How does it react with (i) phenylhydrazine (ii) acetyl chloride (iii) hydroxylamine (iv) dil. caustic soda and (v) ammoniacal silver nitrate ?

3. Outline the preparation of glucose in industry. What are its physical and chemical properties ? What evidence would you put forth to show that glucose has a straight chain structure.

4. Glucose behaves as an alcohol and as an aldehyde ? Do you agree with this statement ? If so, why ?

5. Describe the manufacture of fructose. Discuss its properties and its constitution.

6. Describe briefly the process employed for manufacture of cane-sugar in India. How will you show that cane-sugar is made up of a molecule of glucose and a molecule of fructose less a molecule of water ?

7. What are mono-, di- and polysaccharides ? Illustrate your answer with examples.

8. What is starch ? How is it prepared industrially ? What are its main reactions and uses ?

You are given 50 per cent solutions of glycerol, cane sucrose, grape sugar and urea in four separate test-tubes. By what tests would you distinguish between them ?

9. (a) How will you convert glucose into fructose and *vice versa*.

(b) How is glucose distinguished from fructose ?

(c) How do glucose and fructose react with (a) reducing agents (b) oxidising agents ?

10. Draw a labelled flow sheet for the manufacture of cane sugar and describe the various stages thereof. (Panjab Inter 1962)

11. Write illustrative but brief notes on (a) Monosaccharides (b) Multiple effect evaporator. (Panjab Inter 1959)

12. What are carbohydrates ? Give the preparation of glucose from (i) sucrose and (ii) starch. How are glucose and fructose converted into each other ?

(Panjab Inter 1955)

13. How is cane sugar extracted from the juice of sugar canes ? Give separately the action of (a) conc. nitric acid (b) conc. sulphuric acid and (c) Fehling solution on cane sugar. (Panjab Inter 1953 S)

14. Describe the manufacture of glucose from starch. Put down the formula of the saccharide. What is the action of (a) acetic anhydride (b) phenyl hydrazine (c) sodium amalgam and water (d) a mild oxidising agent (e) ammoniacal silver nitrate and (f) hydroxylamine on glucose. (Panjab Inter 1950 S, 49 S)

AROMATIC COMPOUNDS

CHAPTER XLII

INTRODUCTORY AND NOMENCLATURE

All the compounds studied in the preceding chapters are termed 'open chain' compounds (as they all possess an open or straight chain structure) or 'aliphatic compounds' (as the earliest members of this class were *fatty acids*).

Another major class consists of compounds obtained first from natural resins, balsams, gum benzoin and essential oils (those of cloves, winter green, cinnamon, vanilla, etc.) Since these compounds possessed a pleasant odour, they were termed **aromatic compounds** (Greek, *aroma* = fragrant smell). All these compounds were found to contain a closed chain of six carbon atoms in their molecules.

The aromatic compounds are different from the aliphatic cyclic compounds (alicyclic compounds) such as cyclopentane, cyclohexane, etc. Quite often, the aromatic compounds are also called **benzenoid compounds**.

Reasons for Separate Treatment of Aromatic Compounds. The following characteristics provide a reasonable basis for the separate treatment of aromatic compounds.

(1) Aromatic compounds contain a higher percentage of carbon than the corresponding aliphatic compounds. Benzene (C_6H_6), for instance, contains 92.3 per cent while the corresponding, paraffin, hexane (C_6H_{14}), contains 83.7 per cent of carbon. They burn with a smoky flame.

(2) All aromatic compounds, contain at least one cyclic or closed ring with a benzenoid character whereas the aliphatic compounds possess an open chain structure.

(3) In spite of the fact that the aromatic compounds are unsaturated, they are surprisingly stable towards common reagents like acids, alkalies, oxidising agents, etc. This stability is attributed to their having the ring structure.

(4) Aromatic compounds, when treated with concentrated sulphuric acid, yield sulphonic acids, this reaction being known to take place only for paraffins higher than hexane.

(5) Aromatic compounds, on treatment with concentrated nitric acid, yield nitro compounds. This reaction is also known to occur normally with paraffins beyond hexane.

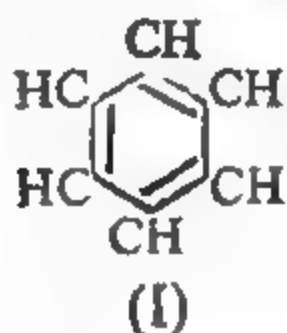
(6) Aromatic hydroxy compounds (phenols) are acidic in nature whereas the aliphatic hydroxy compounds (alcohols) are neutral.

(7) Aromatic amino compounds react with nitrous acid at low temperatures, to yield diazo compounds. This reaction is not known to occur in aliphatic series. Aliphatic amines on treatment with nitrous acid yield alcohols.

(8) Aromatic hydrocarbons form both addition and substitution compounds with halogens whereas the paraffins form only substitution products. Further, while the alkyl halides easily undergo replacement, the aryl halides (aromatic halogen compounds) are very stable and do not normally undergo replacement reactions.

(9) Aromatic compounds undergo typical reactions such as Friedel and Craft's reaction Perkin's reaction, Sandmeyer's reaction, etc., which are not known in aliphatics.

Representation of Benzene. Just as aliphatic compounds are derived from the parent compounds, methane and its homologues, the aromatic compounds are derived from benzene and its homologues. Benzene is represented as a symmetrical hexagonal ring consisting of six carbon atoms in one plane with alternate single and double bonds, each carbon atom carrying one hydrogen atom as shown in representation (I). For the sake of convenience, benzene is usually represented by a regular hexagon with alternate single and double bonds; carbon and hydrogen atoms being assumed to be present at each corner [representation (II)]. Sometimes benzene may also be represented by a plane hexagonal ring; the alternate single and double bonds, carbon and hydrogen atoms being assumed to be present [representation (III)]. This representation should, be discouraged as it, in fact, depicts cyclohexane.



More recently, benzene has been represented by a hexagon containing a dotted circle (IV). It is better than I (or II) in that it emphasizes the equivalence of the six carbon-carbon bonds as well as the extraordinary stability of benzene. However, keeping in view the suggestions received from majority of fellow teachers, formula II will be used in the present volume.

Nomenclature. Like aliphatic compounds, the aromatic compounds also form number of different homologous series such as aldehydes, ketones, acids, hydroxy derivatives, etc.

The nomenclature of these compounds has been discussed below :

(1) **Aromatic hydrocarbons.** Aromatic hydrocarbons form a series of compounds having the general formula, C_nH_{2n-6} where n is equal to 6 or more than 6.

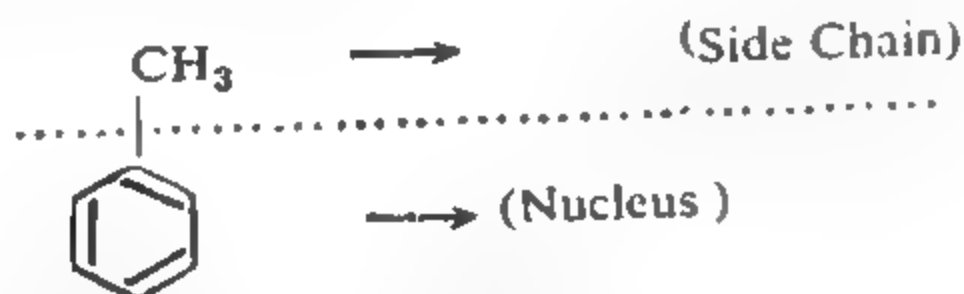
The first member, C_6H_6 , is benzene, the second member, $C_6H_5-CH_3$, is toluene or methyl benzene, and the third member, $C_6H_4\begin{matrix} \nearrow CH_3 \\ \searrow CH_3 \end{matrix}$ is xylene or dimethyl benzene. Similarly, $C_6H_3(CH_3)_3$ is mesitylene or trimethyl benzene.

Every homologue of benzene consists of two parts ;

(a) *Nucleus*

(b) *Side Chain*

For instance, in case of toluene, we have :



It must be borne in mind that a *side chain must always contain at least one carbon atom*. Thus, a hydroxyl group, a nitro group, or an amino group, attached to the benzene nucleus does not constitute a side chain.

Similarly, the groups $-\text{CHO}$, $-\text{COOH}$, attached to the nucleus do not form a side chain. *In fact, a side chain implies an alkyl or a substituted alkyl group*. For instance, $-\text{CH}_3$, CH_2OH , $-\text{CH}_2\text{R}$, are all side chains.

The replacement of any one of the hydrogen atoms in the benzene nucleus by a monovalent atom or group is called **nuclear substitution** and the replacement of any of the hydrogen atoms of the side chain by a monovalent atom or group is known as **side chain substitution**.

These two types of substitutions by the same group in the same compound often give rise to products quite different from one another.

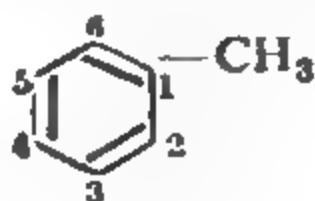
Aromatic Groups. Like aliphatic hydrocarbons, the aromatic hydrocarbons also form monovalent, divalent groups by the loss of one, two or three hydrogen atoms respectively. For example,

C_6H_5- and $\text{C}_6\text{H}_5\text{CH}_2-$ are monovalent groups called *phenyl* group and *benzyl* group respectively. Another monovalent group, $\text{CH}_3\cdot\text{C}_6\text{H}_4-$, is *tolyl* group.

Similarly $\text{C}_6\text{H}_5\text{CH}<$, *benzal*, and $\text{C}_6\text{H}_4<$, *phenylene* are divalent groups. And $\text{C}_6\text{H}_5\text{C}<-$, *benzo* is a trivalent group.

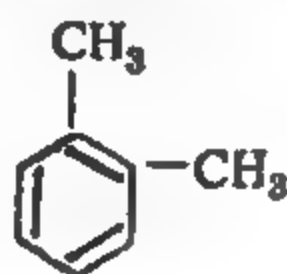
The aromatic monovalent groups such as phenyl (C_6H_5-), tolyl ($\text{CH}_3\text{C}_6\text{H}_4-$), benzyl ($\text{C}_6\text{H}_5\text{CH}_2-$), etc., are known as **aryl groups** (cf. alkyl groups).

Isomerism in Benzene Derivatives. As stated earlier, a benzene molecule is represented by a regular hexagon with six carbon atoms (lying at the corners) in one plane. All the hydrogen atoms are equivalent hence only one mono-substitution product of the type, $\text{C}_6\text{H}_5\text{X}$, is possible ; X being any monovalent atom or group. Thus, there is only one toluene as shown in the formula. The various carbon atoms in the benzene ring are numbered as shown below :

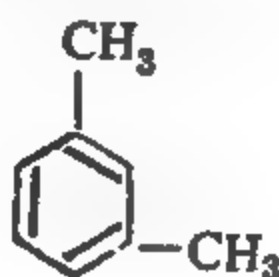


The numbers are assigned in a regular order in such a way that the substituents take the least possible numbers. As in the above formula of toluene, the carbon atoms are numbered in a clockwise manner.

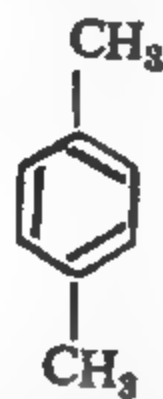
The next homologue, xylene or dimethyl benzene, can be obtained by replacing any one of the remaining five hydrogen atoms of the benzene nucleus by a methyl group. A little consideration will show that only three xylenes are possible, viz.,



(i)

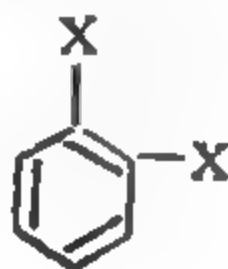


(ii)

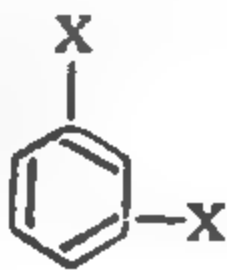


(iii)

These three structures are respectively named as *ortho*-xylene (or 1 : 2 dimethyl benzene), *meta*-xylene (or 1 : 3 dimethyl benzene) and *para*-xylene (or 1 : 4 dimethyl benzene), as disubstituted 1 : 5- and 1 : 6- structures are identical with 1 : 3- and 1 : 4- disubstituted compounds respectively. Thus, benzene is capable of forming three disubstituted derivatives of the type $C_6H_4X_2$ (where X is a monovalent group) having the structures.

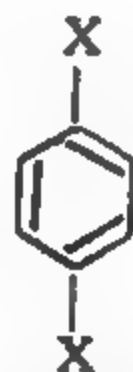


1 : 2 Disubstituted
derivative
or *ortho*-derivative



1 : 3 Disubstituted
derivative or
meta-derivative

and



1 : 4 Disubstituted
derivative or
para-derivative

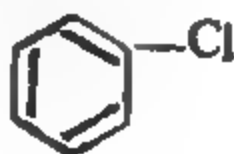
These are generally written as *o*—, *m*—, and *p*— derivatives, respectively.

In other words, three isomeric compounds, with the same molecular formula, $C_6H_4X_2$, are possible.

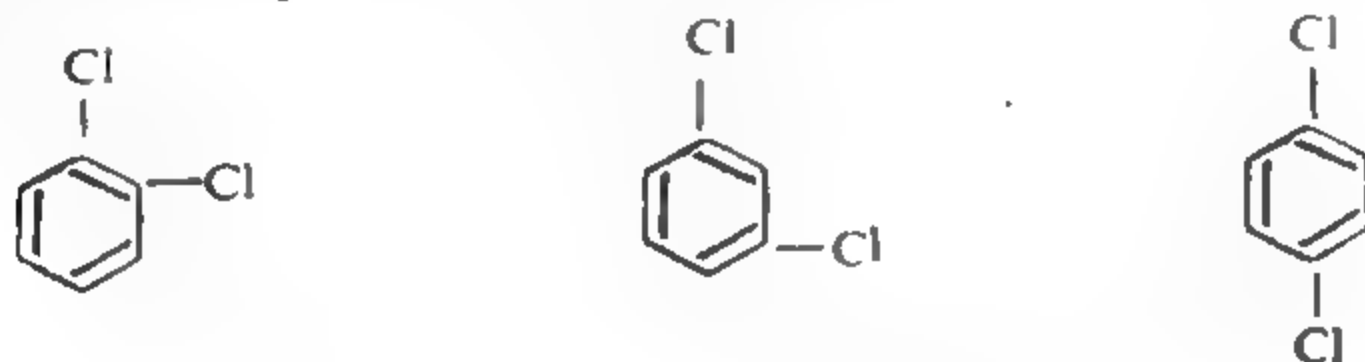
This type of isomerism, which is due to different positions occupied by the substituent groups in the benzene ring, is called **position isomerism**. Thus, three xylenes, three dichlorobenzenes, three chlorotoluenes are theoretically possible.

2. (i) **Halogen derivatives of benzene.** The compounds obtained by the replacement of one or more hydrogen atoms of the benzene ring by the halogen atoms are called halogen derivatives of benzene. For example,

Monochlorobenzene (or simply chlorobenzene) or phenyl chloride, C_6H_5Cl , is represented as :



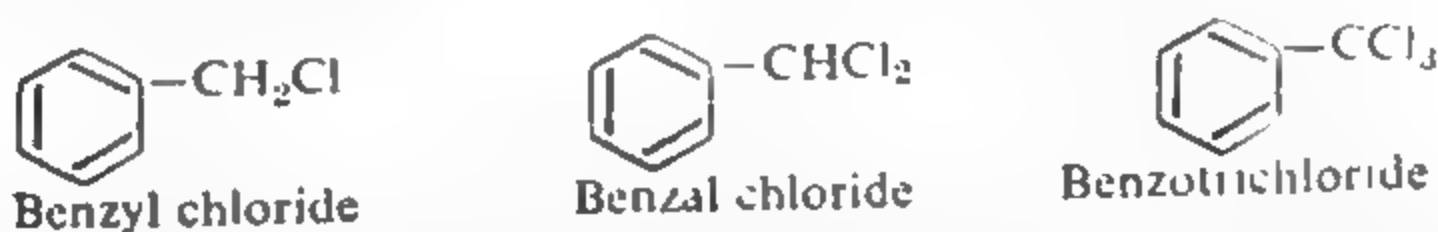
Dichlorobenzene, $C_6H_4Cl_2$, can exist in three isomeric forms, viz., ortho, meta and para, as represented below :



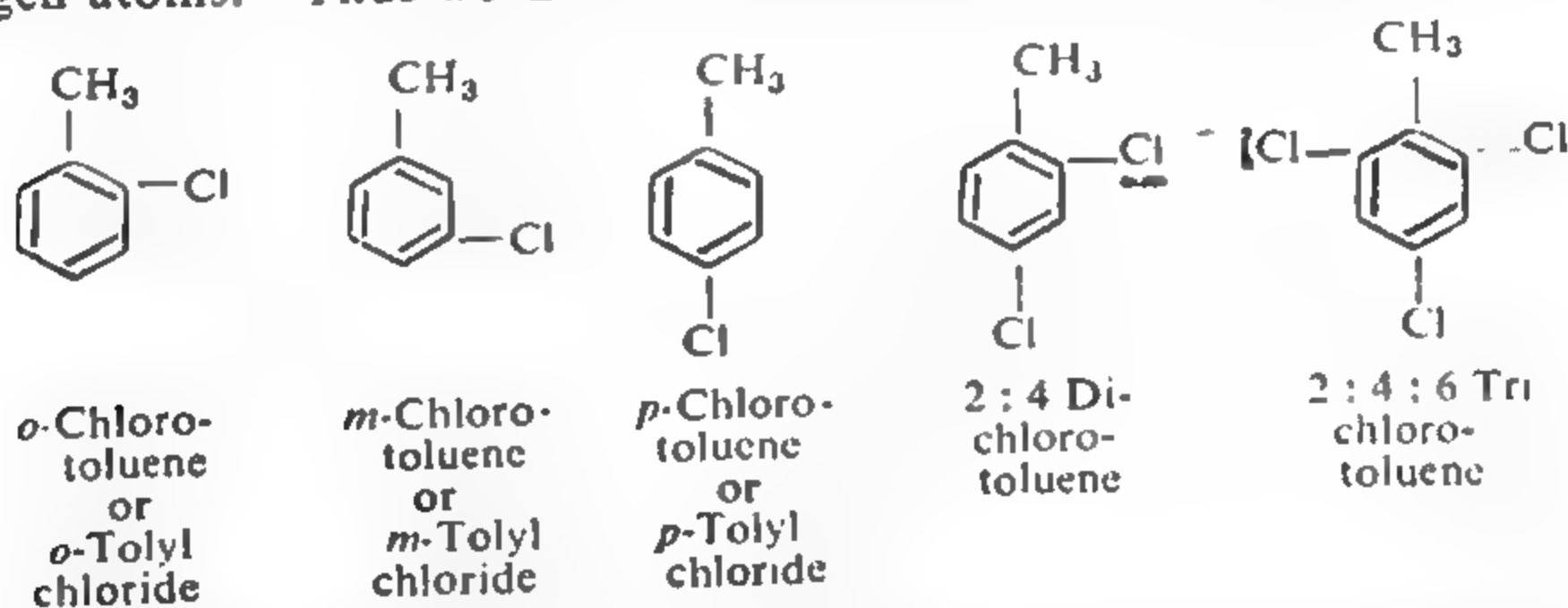
o-Dichlorobenzene *m*-Dichlorobenzene *p*-Dichlorobenzene

(ii) **Halogen derivatives of toluene.** It will now be clear that toluene $C_6H_5.CH_3$, can yield two types of halogen derivatives, viz. (a) *side chain substituted* and (b) *nuclear substituted*.

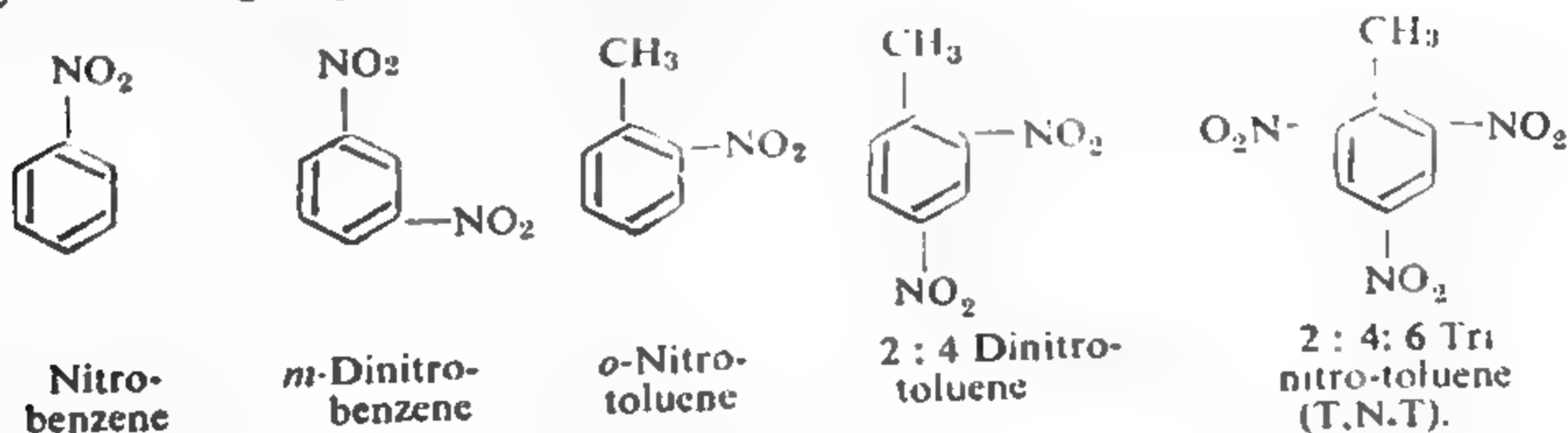
(a) *Side chain substituted derivatives.* These are obtained by the substitution of one or more hydrogen atoms of the side chain by one or more halogen atoms. Thus we have :



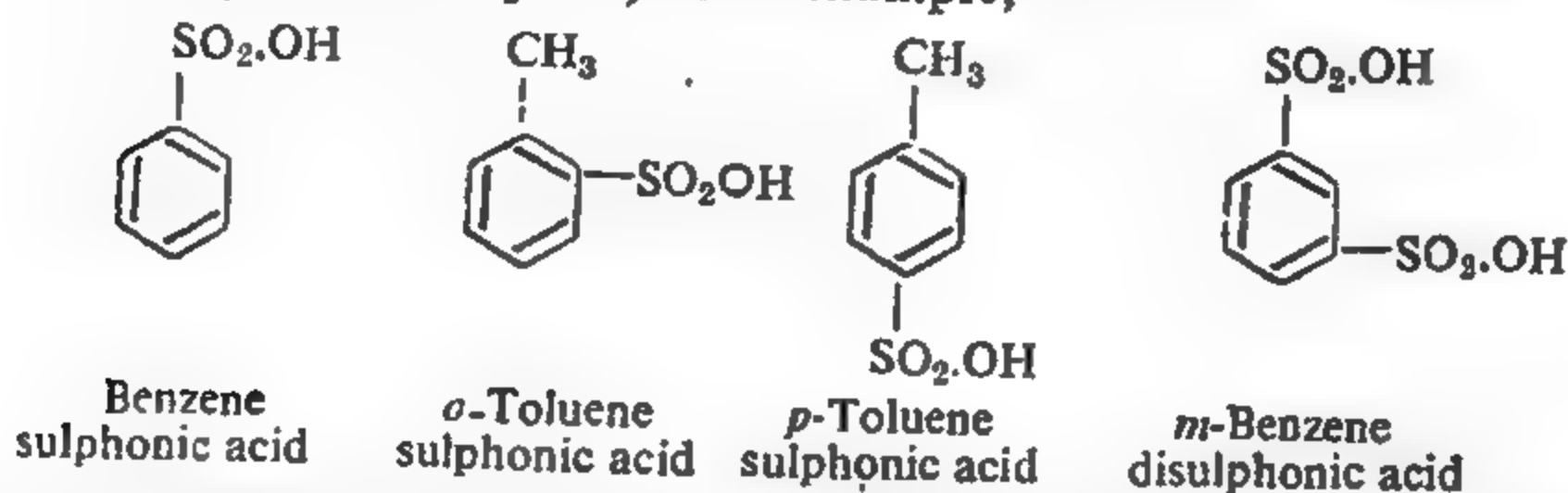
(b) *Nuclear substituted derivatives.* These are formed by the replacement of one or more hydrogen atoms of the benzene nucleus by halogen atoms. Thus we have :



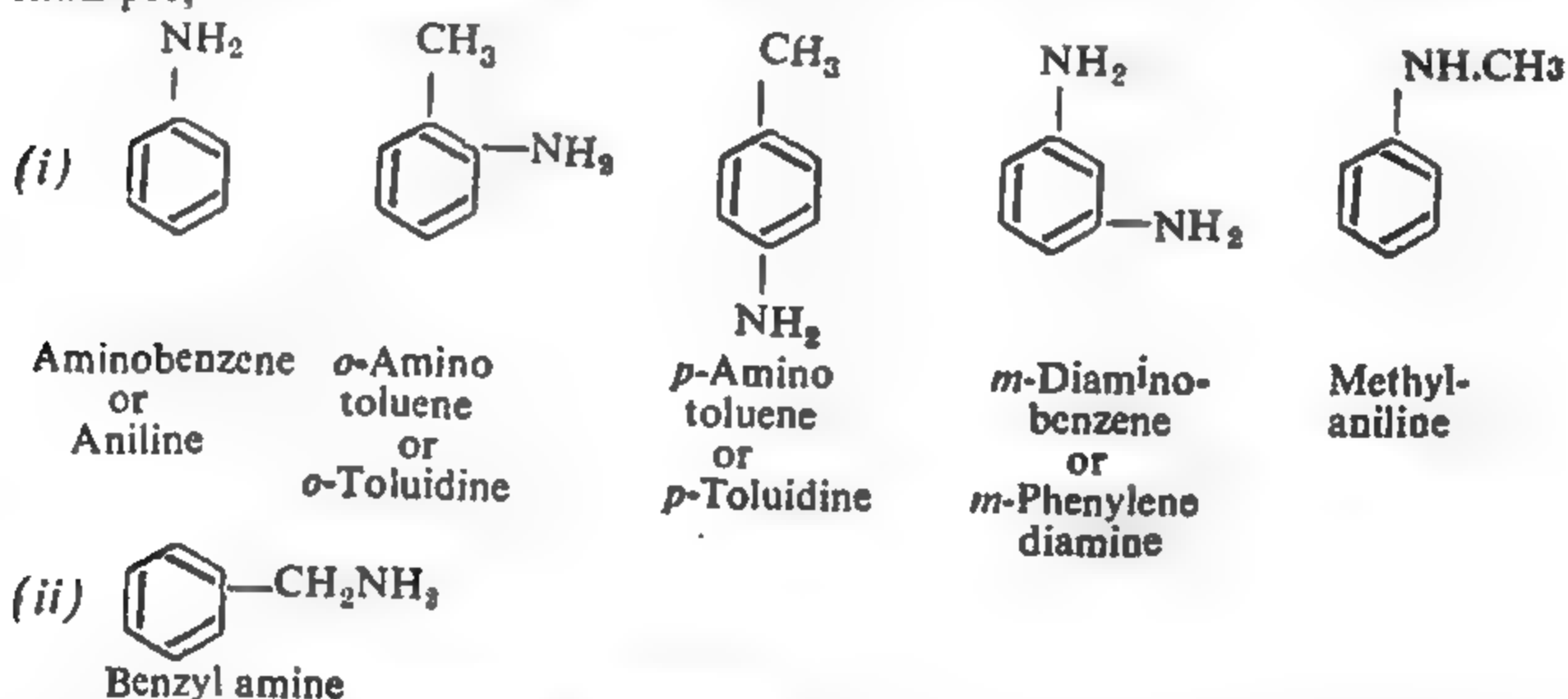
(3) **Nitro Derivatives.** Aromatic nitro derivatives are obtained by the replacement of one or more hydrogen atoms of the benzene nucleus by the nitro groups. For instance.



(4) **Sulphonic acids.** Aromatic sulphonic acids are obtained by the replacement of one or more hydrogen atoms of the nucleus by sulphonic acid group (*i.e.*, $-\text{SO}_2.\text{OH}$). For example,



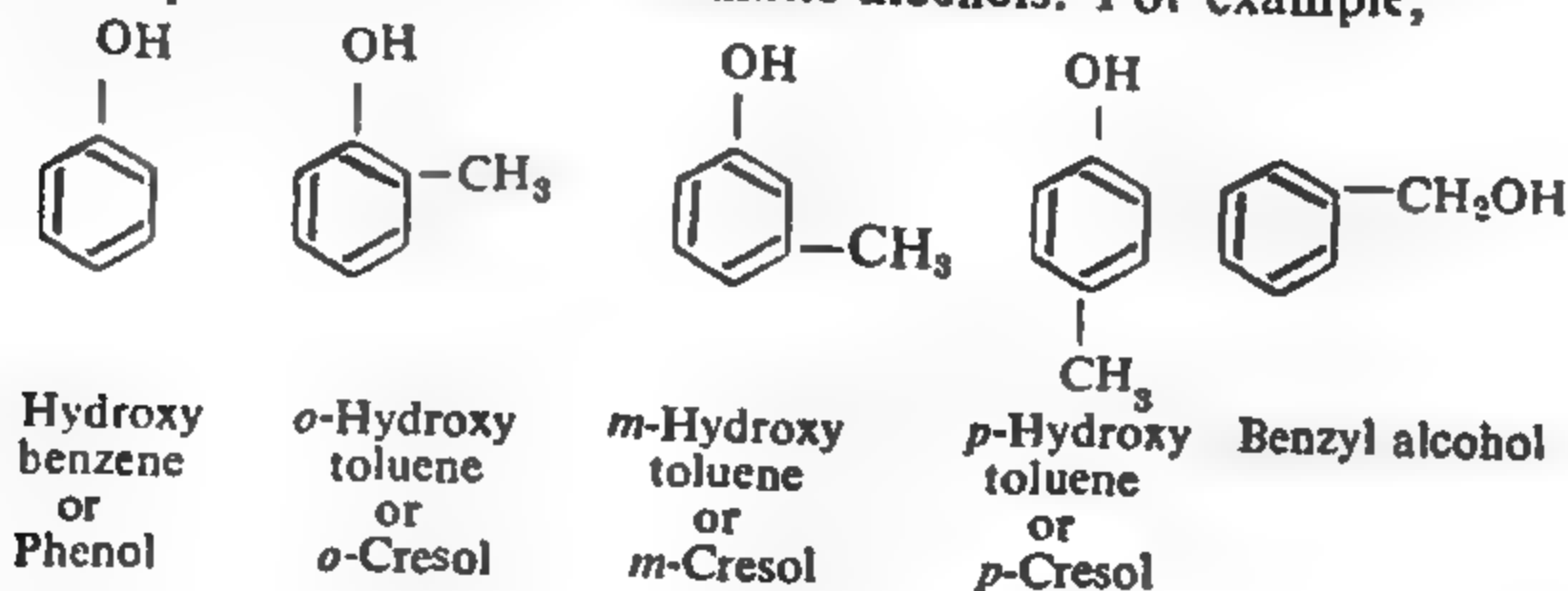
(5) **Amino derivatives.** Two types of amino derivatives are possible depending upon whether the nuclear hydrogen atom or a hydrogen atom of the side chain is replaced by an amino ($-\text{NH}_2$) group. For example,



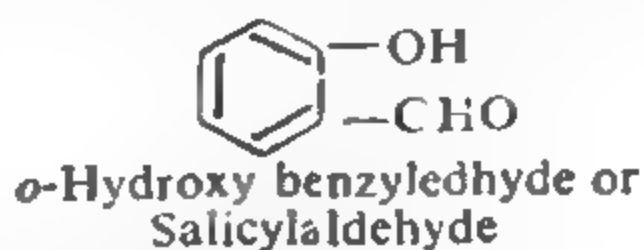
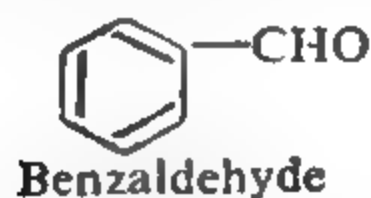
(6) **Diazo-compounds or diazonium salts.** These are obtained by the replacement of nuclear hydrogen atom by a diazo group, $-\text{N}=\text{N}\text{X}$ (where X is an anion, *e.g.*, $-\text{Cl}$, $-\text{HSO}_4$) generally called a diazonium group. For instance,



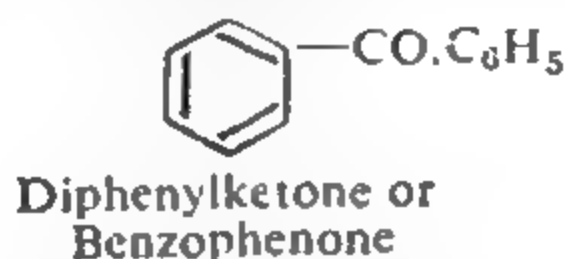
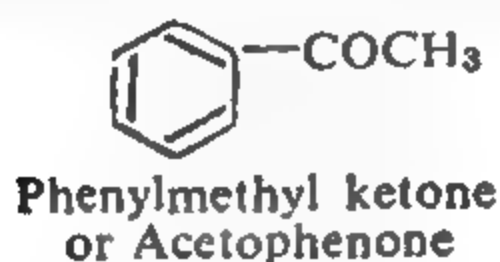
(7) **Aromatic hydroxy compounds.** The nuclear hydroxy derivatives of aromatic hydrocarbons are known as phenols and the side chain substituted compounds are called aromatic alcohols. For example,



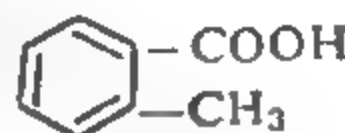
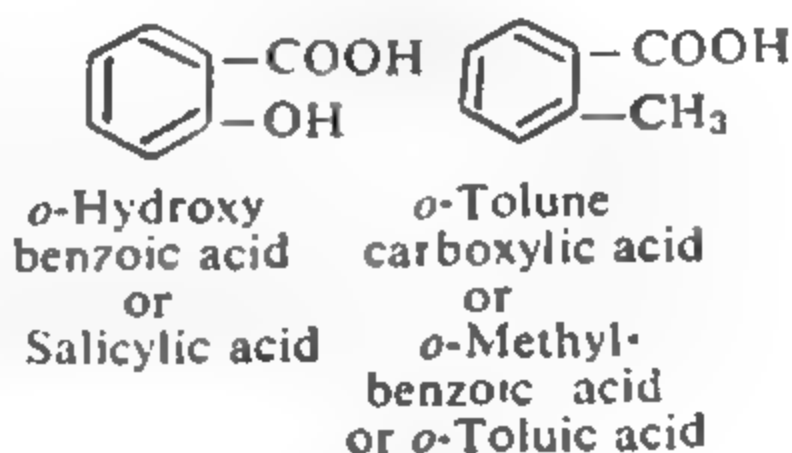
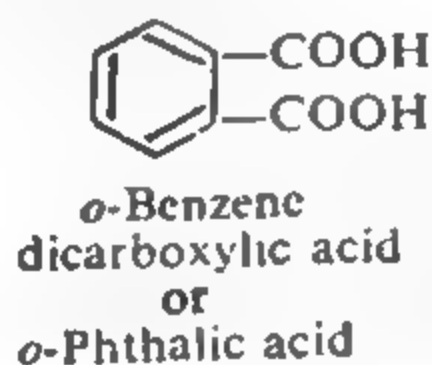
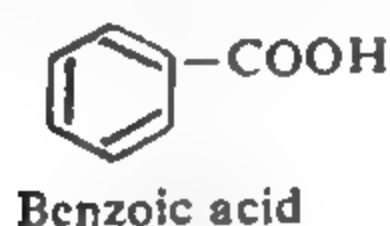
(8) **Aromatic aldehydes.** These compounds contain an aldehydic group directly linked to the benzene nucleus and are named after the name of the acid they produce on oxidation. For example,




(9) **Aromatic ketones.** Here the ketonic group ($>\text{C}=\text{O}$) is directly linked to the benzene nucleus. For instance,

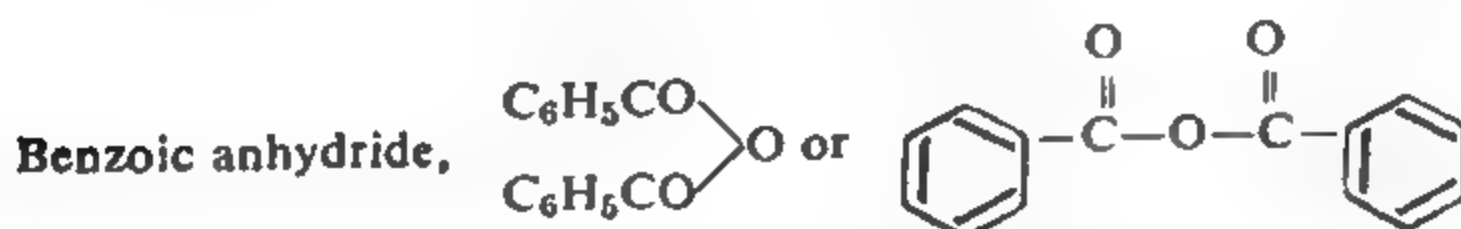


(10) **Aromatic carboxylic acids.** These are obtained by the replacement of one or more hydrogen atoms of the benzene nucleus by the carboxyl groups. For example,



The group, $\text{C}_6\text{H}_5\text{CO}-$, , is called the benzoyl group.

(11) **Derivatives of carboxylic acids.** Just as the fatty acids form acid derivatives (such as acid chlorides, acid amides, anhydrides, esters) the aromatic acids, too, form similar compounds. For example,



QUESTIONS

1. Define the terms 'Nucleus' and 'Side Chain' as applied to aromatic compounds. Illustrate your answer with examples.

2. What do you understand by the term 'aromatics'? What are the distinguishing features of such compounds as compared to their aliphatic counterparts?

3. Explain the following :

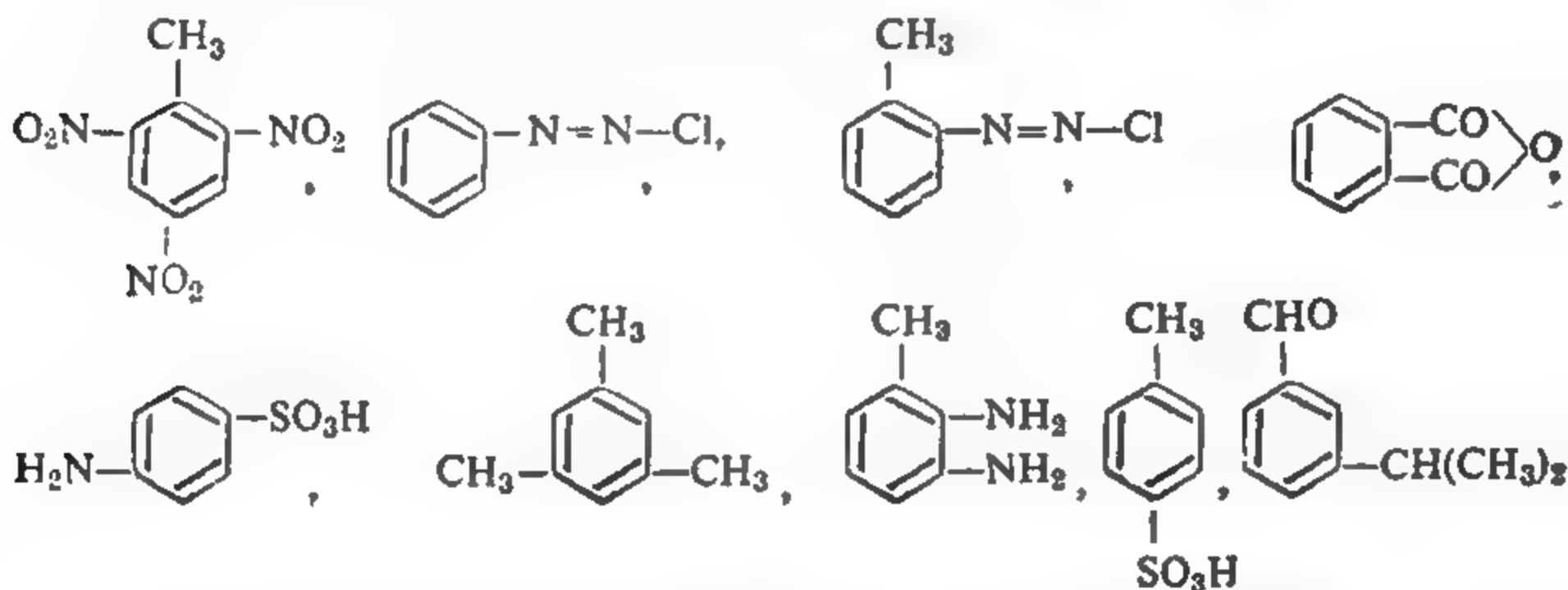
Ortho, para, and meta as applied to aromatic compounds. Illustrate your answer with at least two examples of each.

4. Write structural formulae for the following :

(i) Aniline (ii) Phenol (iii) *p*-Chlorotoluene (iv) *m*-Dinitrobenzene (v) 2 : 4 : 6-Trinitrobenzene (vi) *o*-Hydroxy benzaldehyde (vii) Benzyl alcohol (viii) Phthalic acid (ix) Benzal chloride (x) *m*-Xylene (xi) Acetophenone (xii) Benzoyl chloride.

5. Define an aryl group. Write the formula and names of common aryl groups

6. Give the names of the following structures :



7. Name the various classes of aromatic compounds, giving the formula and name of at least one member of each class.

8. How many isomers are possible in case of (i) Monosubstituted benzene. (ii) Disubstituted benzene? Give reasons for your answer in the two cases. (Panjab Inter 1953)

9. What do you understand by the term : Ring and chain substitutions? (Panjab Inter 1952)

10. What is meant by the term : side chain?

Give a few instances of compounds containing side chain.

(Panjab Inter 1948)

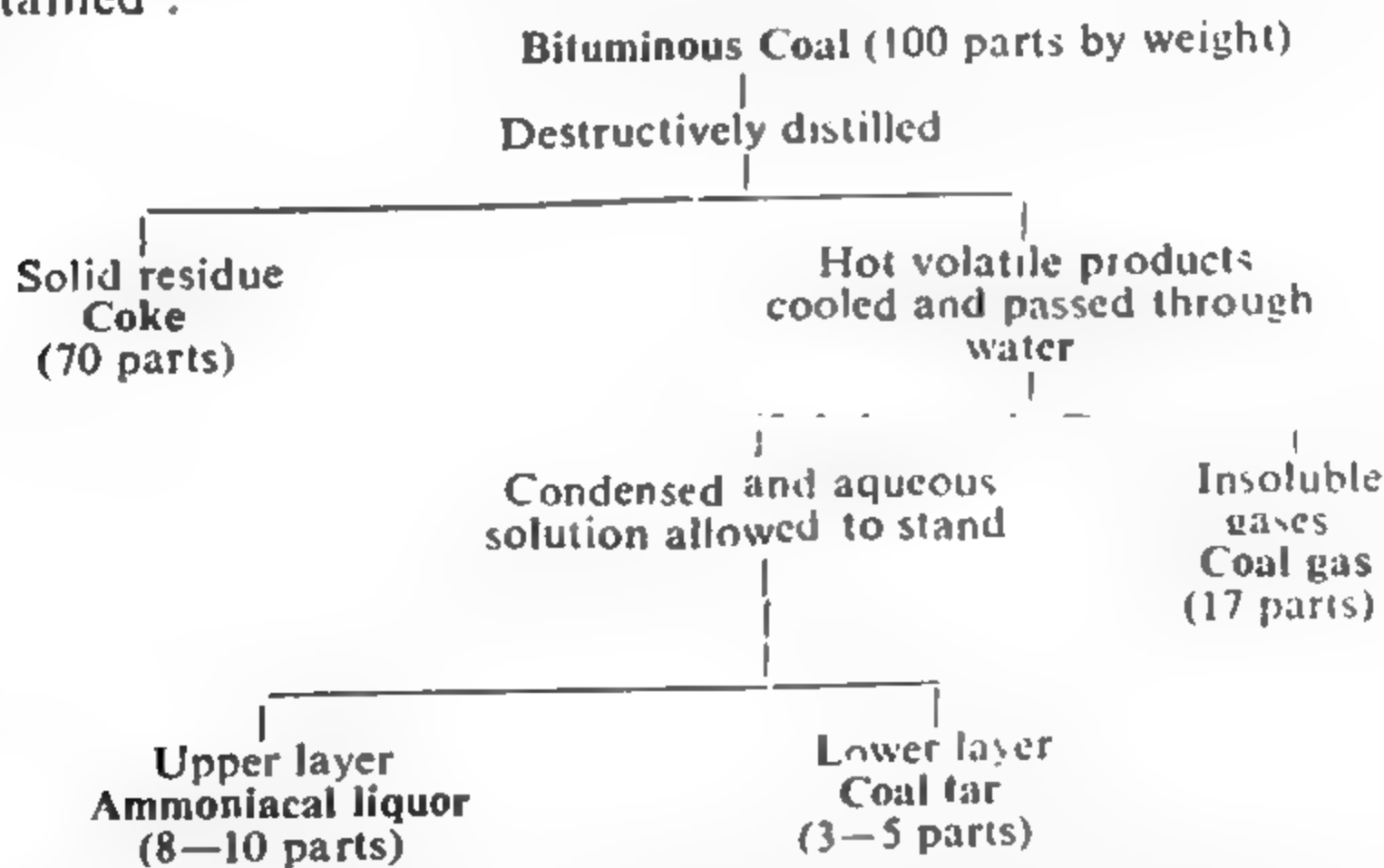
CHAPTER XLIII

COAL TAR AND ITS PRODUCTS

Aromatic compounds are widely distributed in nature, in plants and animals but the most important and abundant source of aromatic compounds is **coal tar**—the dark viscous liquid obtained during the destructive distillation of coal at temperatures above 1000° .

Coal and its Destructive Distillation. The slow decomposition of wood under high pressure and high temperature, in the interior of the earth, produces coal which is a mixture of complex organic compounds along with free carbon. Bituminous coal, for instance, contains about 30—40 per cent of volatile matter.

Coal is destructively distilled (*i.e.*, strongly heated out of contact with air) in fire clay or iron retorts at $1,000-1,400^{\circ}$. The following products are obtained :



The destructive distillation of coal is carried out chiefly for two purposes : (a) for the production of coke required for the metallurgy of iron and (b) for the manufacture of coal gas needed as a household fuel.

Recently, a new process for the carbonization (*i.e.*, destructive distillation) of coal has been put into use. This process, known as the low temperature carbonization

consists in heating coal at 600° under reduced pressure, when a smokeless fuel, *coalite* is obtained. This process yields less volume of coal gas but the amount of coal tar is doubled. This coal tar contains a predominating percentage of aliphatic hydrocarbons, from which motor spirit is made.

Distillation of Coal Tar. The coal tar is a black viscous oily liquid possessing an unpleasant smell. At one time, it was considered to be a waste and a veritable nuisance, but today it is an extremely important source of a large variety of raw materials for the manufacture of a number of important products such as drugs, dyes, perfumes, explosives plastics, etc.

Coal tar is a complex mixture of organic substances and suspended free carbon with varying amounts of water. The main constituents present in coal tar are :

Neutral substances : Benzene, toluene, xylenes, naphthalene, anthracene.

Acidic substances : Carboic acid (phenol) and cresols.

Basic substances : Pyridine, quinoline, etc.

The various substances present in coal tar are isolated by fractional distillation. A diagram of the distillation plant is shown in Fig. 1.

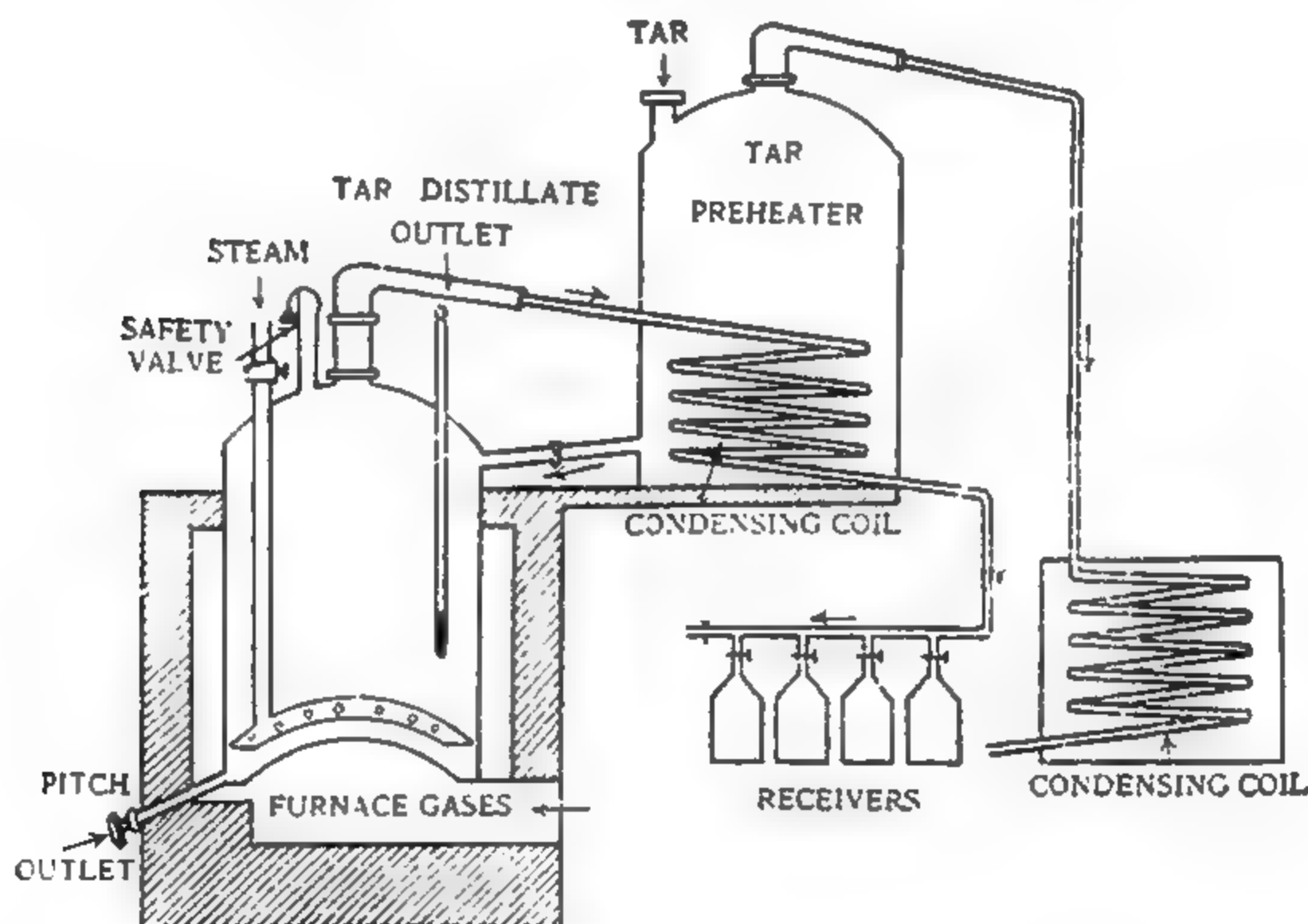


Fig. 1. Distillation of Coal Tar.

The first step is to eliminate water from the coal tar. This is essential as otherwise the water will cause a lot of undesirable frothing during the distillation. For this purpose, coal tar is first taken in a 'pre-heater' having a set of condensing coils carrying hot vapours from the iron still (Fig. 1). This heat is utilised in evaporating off the water present in coal tar. The water vapour obtained herein also carry along some low boiling hydrocarbons and are condensed in the condensing

pipes immersed in water as shown on the extreme right of the figure. The dehydrated tar is then led into a large dome-shaped vertical wrought iron still, (capacity 15–20 tons) with a raised bottom and heated by direct fire. The iron still is also fitted with a steam coil, a thermometer and a worm condenser which is passing through the preheater. The various fractions distilling over at different temperature ranges are collected in different receivers. Towards the end of the operation, a black mass called **pitch** is left in the still. In order to prevent its caking, steam is passed through the steam pipe. The raised bottom helps in draining out the pitch easily and also in carrying heat into the interior of the mass. The various fractions obtained along with their temperature ranges and the compounds they contain are given in Table 1.

TABLE 1
Products of Coal Tar Distillation

S.No.	Name of the fraction	Temperature range	Approximate yield (%)	Principal components
1.	Light oil or crude naphtha	up to 170°	2.5	Benzene, toluene, xylene.
2.	Middle oil or carbolic oil.	170–230°	8–10	Phenol and naphthalene.
3.	Heavy oil or creosote oil.	230–270°	8–10	Naphthalene, naphthol and cresols.
4.	Green oil or anthracene oil.	270–400°	16–20	Anthracene.
5.	Pitch (residue).		50–60	Carbon.

(1) **Light Oil or Crude Naphtha.** (Up to 170°). This fraction is so named as it is lighter than water. It contains mostly neutral hydrocarbons, benzene, toluene, xylene along with a little of thiophene. Besides these, some phenol and pyridine are also present. The light oil is washed successively with sulphuric acid, water, sodium hydroxide and water. The acid treatment removes basic substances like pyridine and also removes a part of thiophene. The alkali treatment eliminates phenols. The washed light oil is then redistilled when the following fractions are obtained :

(i) 90% Benzol (up to 110°)

(ii) 50% Benzol (110–140°)

(iii) Solvent naphtha or benzine (140–170°)

(i) The 90% Benzol contains about 70% benzene, 24 per cent toluene and the rest is xylene. It is called 90% benzol because 100 ml. of this fraction when distilled up to 100° yields a distillate measuring 90 ml. This is the most important source of benzene.

Recovery of benzene. The '90% benzol' is subjected to fractional distillation and the fraction passing over between 80–82° is collected. It gives almost pure benzene and can be put to commercial use as such.

Alternatively, the middle oil fraction is cooled, when naphthalene separates out. It is purified as above. The mother liquor containing phenol and cresols is treated with sodium hydroxide solution when phenol and cresols dissolve as sodium salts. The aqueous layer is separated and acidified with dilute sulphuric acid when phenol and cresols are regenerated. The oily layer is separated, washed, dried and distilled fractionally to separate the phenols.

Phenol is used for preparing explosives, dyes, disinfectants, bakelite plastics, etc. Naphthalene is employed for the manufacture of dyes and drugs.

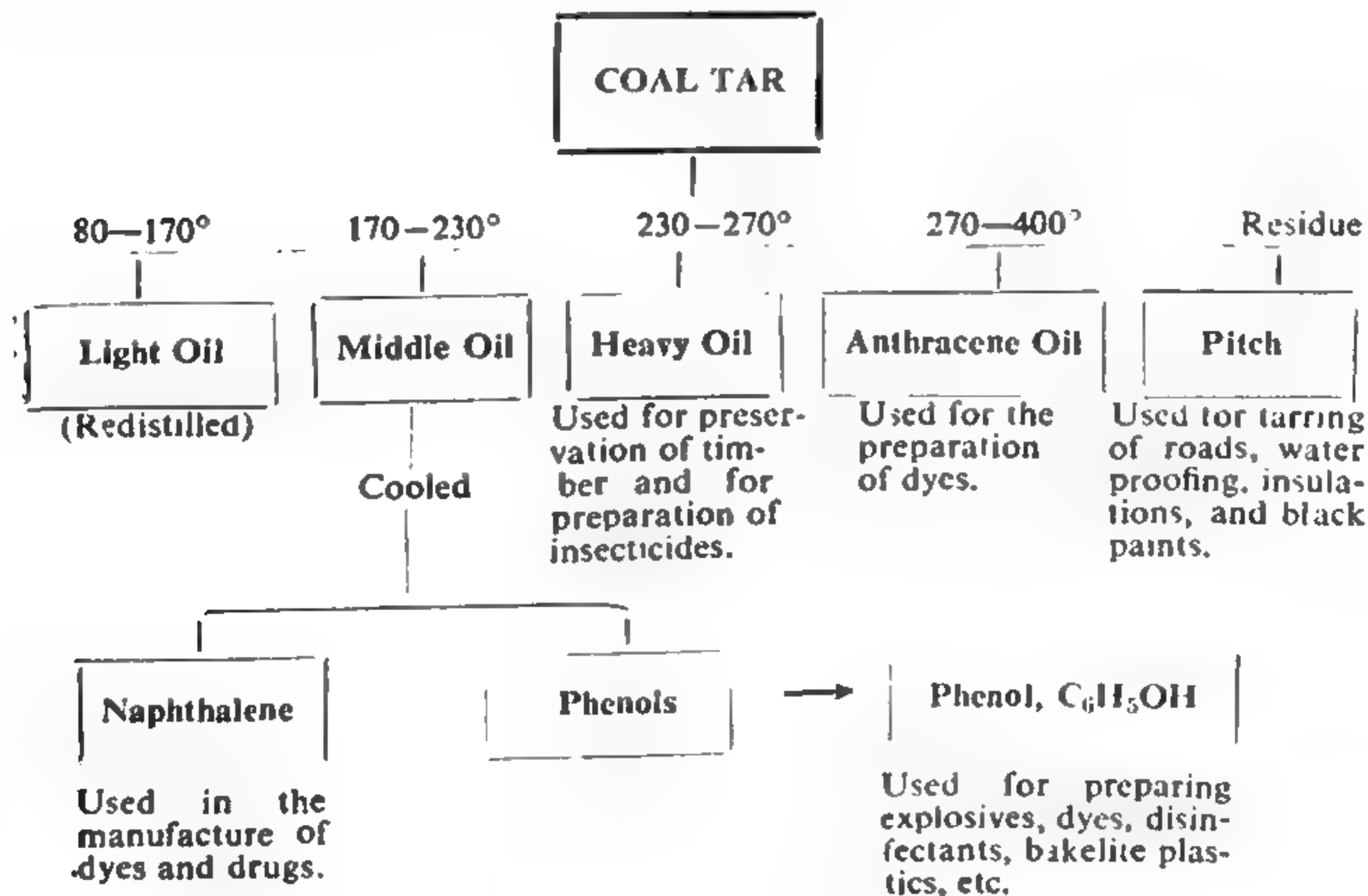
(3) **Heavy oil or Creosote oil (230—270°).** This fraction is heavier than water and hence its name. It is not subjected to any treatment and is used as such for preservation of timber and preparation of insecticides.

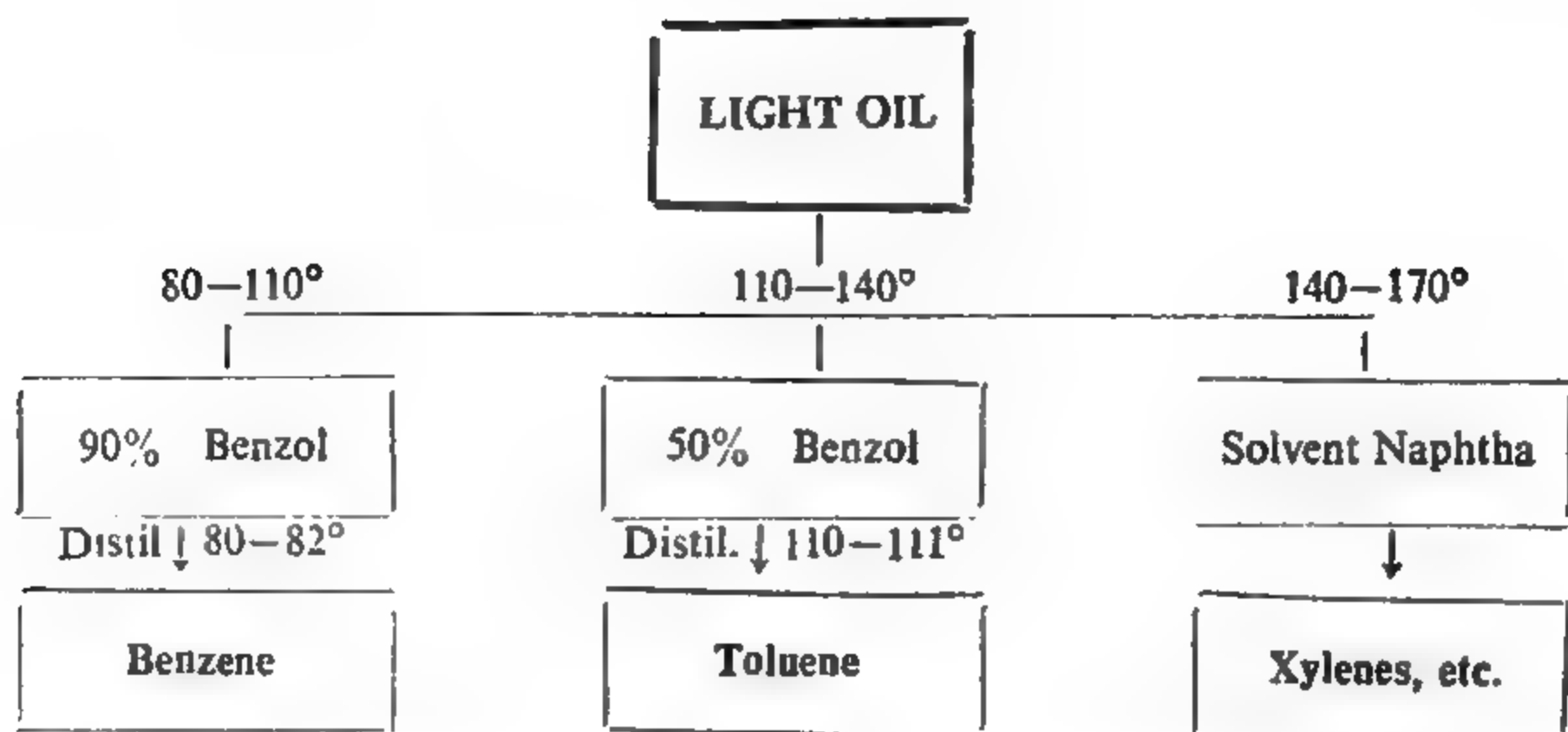
(4) **Anthracene oil or Green oil (270—400°).** This fraction contains mainly anthracene which crystallises out on cooling. It is separated by vacuum filtration, purified and used for the preparation of dyes.

(5) **Pitch.** The pitch is used for tarring of roads. It is also used for water-proofing and in making acid-resistant stone-ware. It also finds application as a binding and insulating material.

It may be of interest to know that one ton of coal yields 10–12 gallons of tar which on proper treatment yields $3\frac{1}{2}$ lb. of benzene and toluene, $1\frac{1}{2}$ lb. of phenol, 6 lb. of cresol, 5–20 lb. of naphthalene and $\frac{1}{4}$ lb. of anthracene.

SUMMARY





QUESTIONS

1. Name the chief sources of aromatic compounds. Describe the main fractions of coal tar distillation.
2. How would you obtain (a) Pure benzene from light oil and (b) Phenol from middle oil?
3. Write an essay on coal tar distillation.
4. "Coal has a special significance for an organic chemist." Discuss and justify this statement.
5. (a) How is phenol isolated from 'middle oil' fraction of coal tar distillation? *(Panjab Inter 1961S)*
(b) Write about 10 lines on light oil fraction of coal tar distillation. *(Panjab Inter 1959 S)*
6. Discuss the Fractional Distillation of coal tar to show that it is an important source of aromatic compounds. *(Panjab Inter 1954)*
7. Describe how pure benzene is obtained from coal tar. *(Panjab Inter 1953, 1948)*
8. How would you purify commercial benzene which was obtained by fractionating 90% benzol? Then, how will you show the absence of impurity in it? *(Panjab Inter 1951 S)*
9. Give an account of the process of isolation of phenol from the middle oil fraction of coal tar. *(Panjab Inter 1951)*
10. Describe the preparation of toluene from 50% benzol. *(Panjab Inter 1941)*

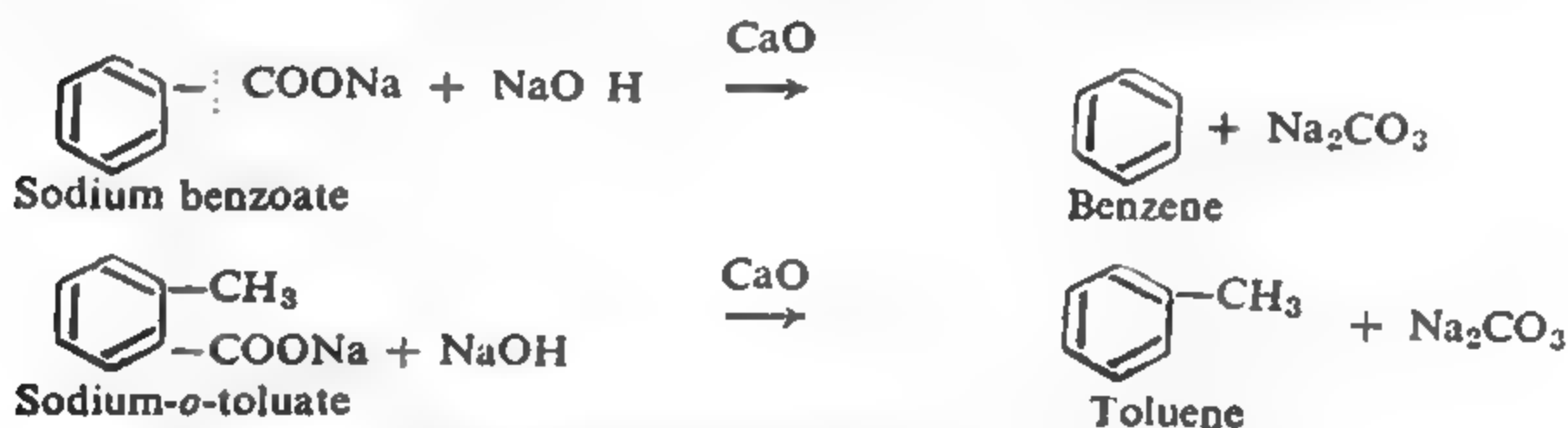
CHAPTER XLIV

BENZENE AND ITS HOMOLOGUES

The parent compound of the aromatic hydrocarbons is benzene, C_6H_6 . The subsequent members are toluene, $C_6H_5.CH_3$, xylene, $C_6H_4(CH_3)_2$, mesitylene, $C_6H_3(CH_3)_3$ and so on. These hydrocarbons can be represented by a general formula C_nH_{2n-6} where n is 6 or a higher number.

These hydrocarbons are present in small amounts in natural petroleum but their chief source is coal tar.

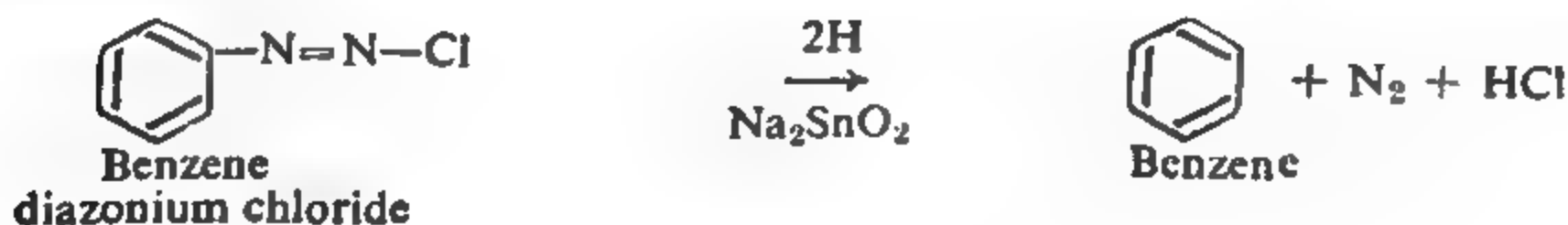
General Methods of Preparation. (1) By distilling sodium salt of the corresponding carboxylic acid with soda lime. For example,

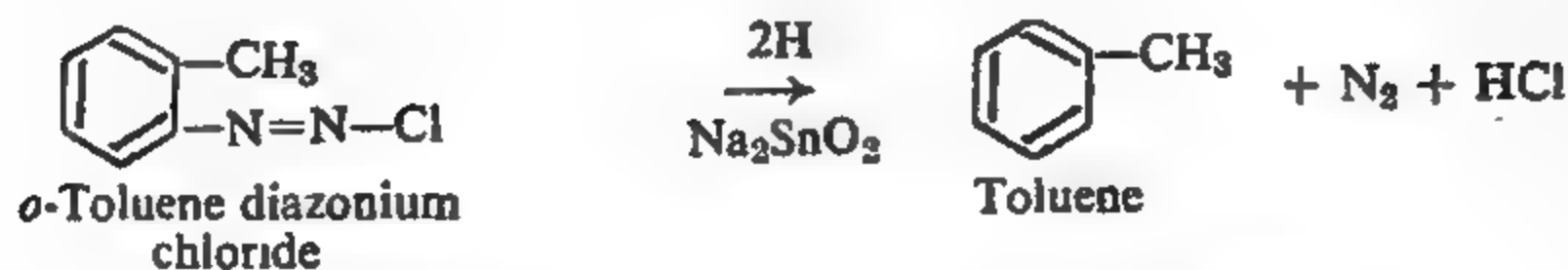


(2) By distilling phenols with zinc dust. For example,

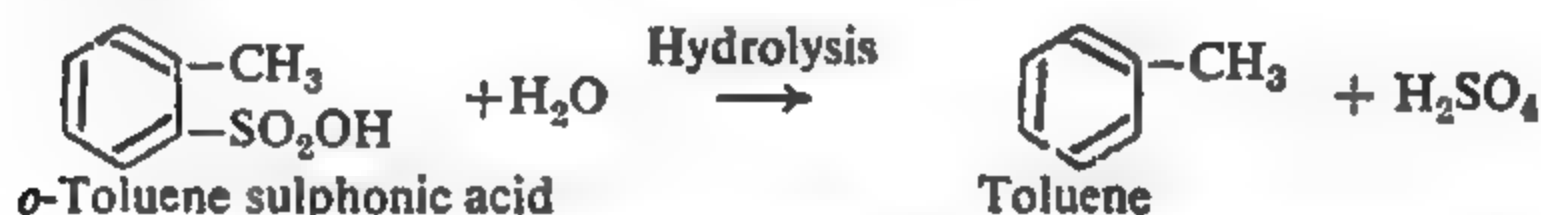
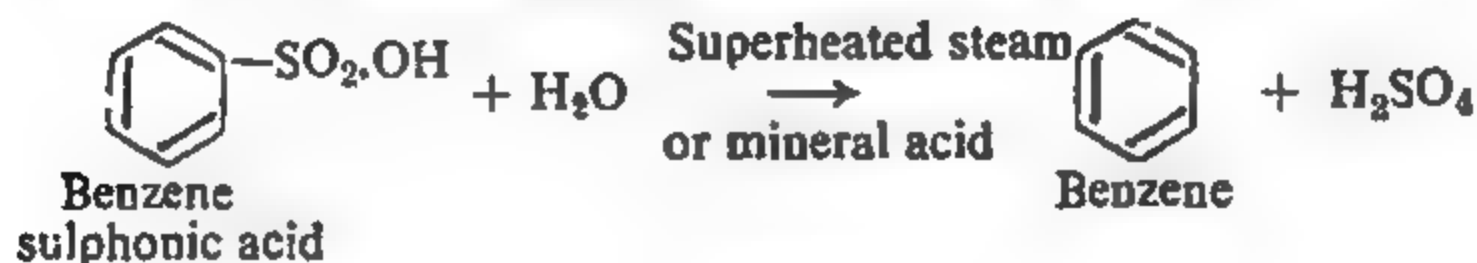


(3) By reducing the corresponding diazonium salt with alkaline sodium stannite.

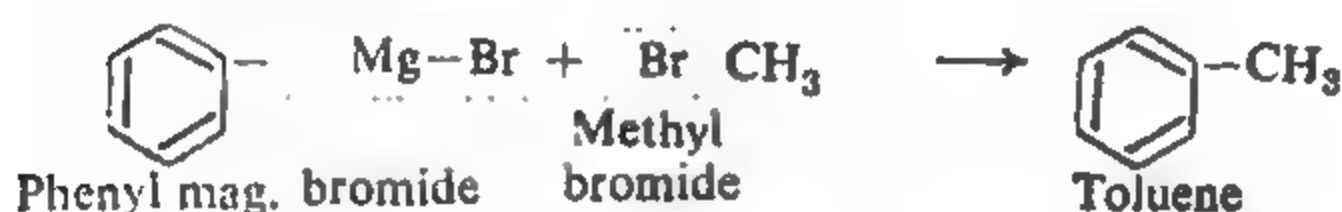




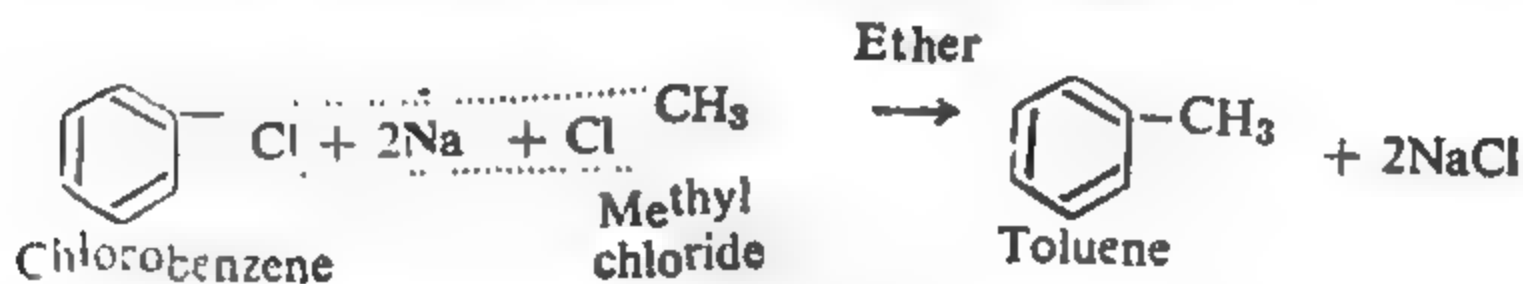
(4) By hydrolysing the corresponding sulphonic acid with superheated steam or by boiling with a dilute mineral acid.



(5) By treating the corresponding Grignard reagent with water or an alkyl halide.

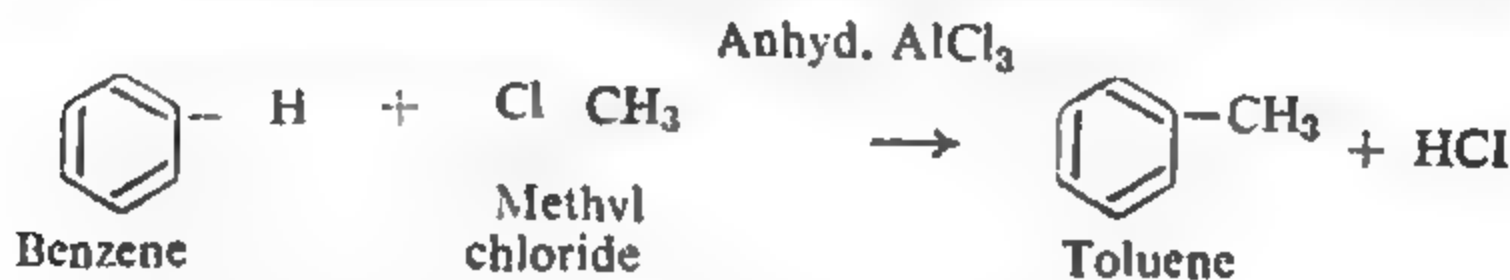


(6) By treating an aryl halide with an alkyl halide in the presence of dry sodium and dry ether (Wurtz-Fittig's reaction).



Benzene cannot be prepared by this method.

(7) By treating benzene with an alkyl halide in the presence of anhydrous aluminium chloride as a catalyst (Friedel and Craft's reaction).



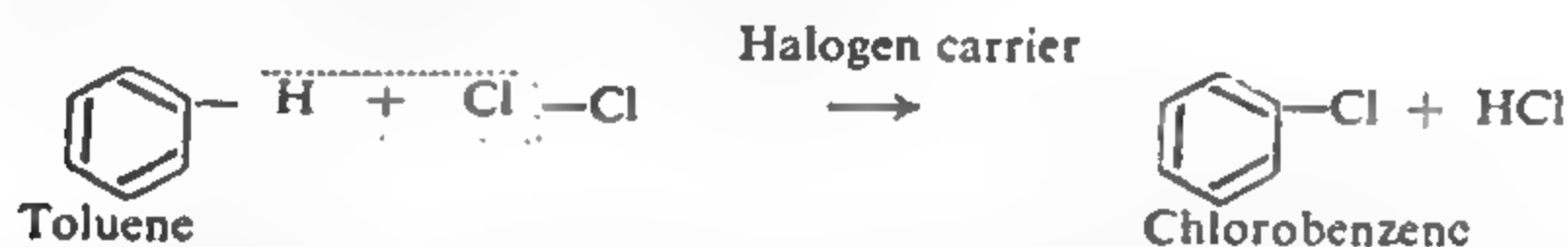
Evidently benzene cannot be prepared by this method also. However, this is the best method for converting benzene into its higher homologues.

Physical Properties. The lower members are colourless highly refracting liquids, with a characteristic aromatic odour. They are immiscible with water but dissolve freely in organic solvents. Their boiling points increase with increase in molecular weights. They are highly inflammable and their vapour are toxic in nature. The lowest members are excellent solvents for oils, fats, resins, sulphur, etc.

Chemical Properties. The benzene ring present in aromatic hydrocarbons is highly stable and is not attacked by any of the reagents, such as acids, alkalies, oxidising agents, etc. The side chains, however, are easily oxidised to carboxylic groups with acidic potassium permanganate. The hydrogen atoms present in the nucleus or in the side chain readily undergo substitution reactions (*cf.* alkanes). The important reactions of aromatic hydrocarbons are :

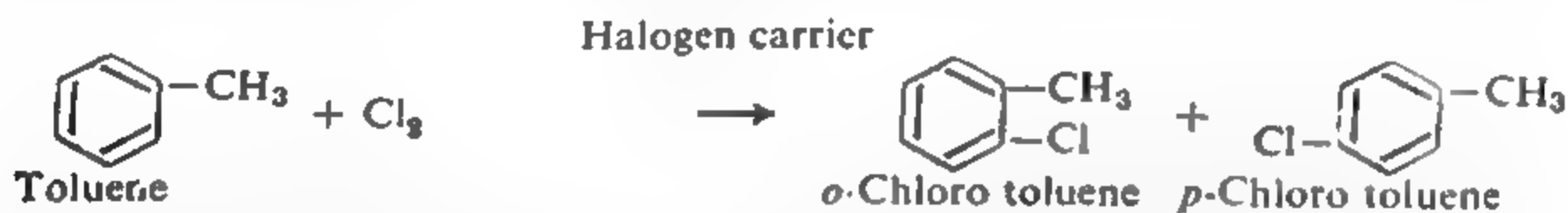
I. Replacement Reactions

(1) **Halogenation.** In the presence of a halogen carrier, like iodine or iron, at ordinary temperatures, nuclear substituted derivatives are formed with chlorine or bromine.

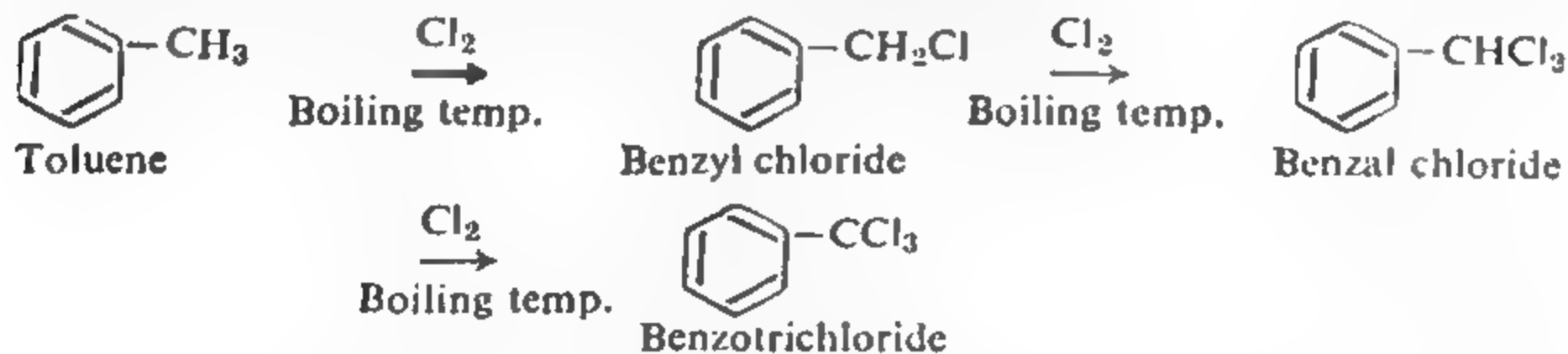


On prolonged treatment, other hydrogen atoms are also successively replaced yielding ultimately hexachlorobenzene, C_6Cl_6 .

With toluene under the above conditions the reaction takes place as under :



In the absence of a halogen carrier and at boiling temperatures, the substitution takes place in the side chain when all the three hydrogen atoms are successively replaced by halogen atoms.

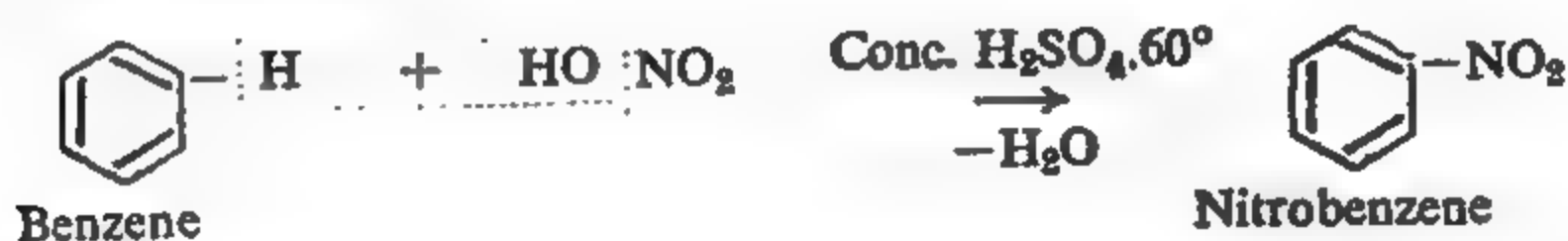


With iodine, the reaction is reversible as the HI formed reduces the iodo derivative back to the parent hydrocarbon. Thus. :



But at high temperatures and in the presence of oxidising agents like iodic acid, hydriodic acid is removed from the sphere of action ($2\text{HI} + \text{O} \rightarrow \text{H}_2\text{O} + \text{I}_2$) and the reaction proceeds to completion yielding iodobenzene.

(2) **Nitration.** With concentrated nitric acid (in the presence of concentrated sulphuric acid), one or more hydrogen atoms of the benzene nucleus are replaced by the nitro ($-\text{NO}_2$) groups. This process is known as *nitration*.

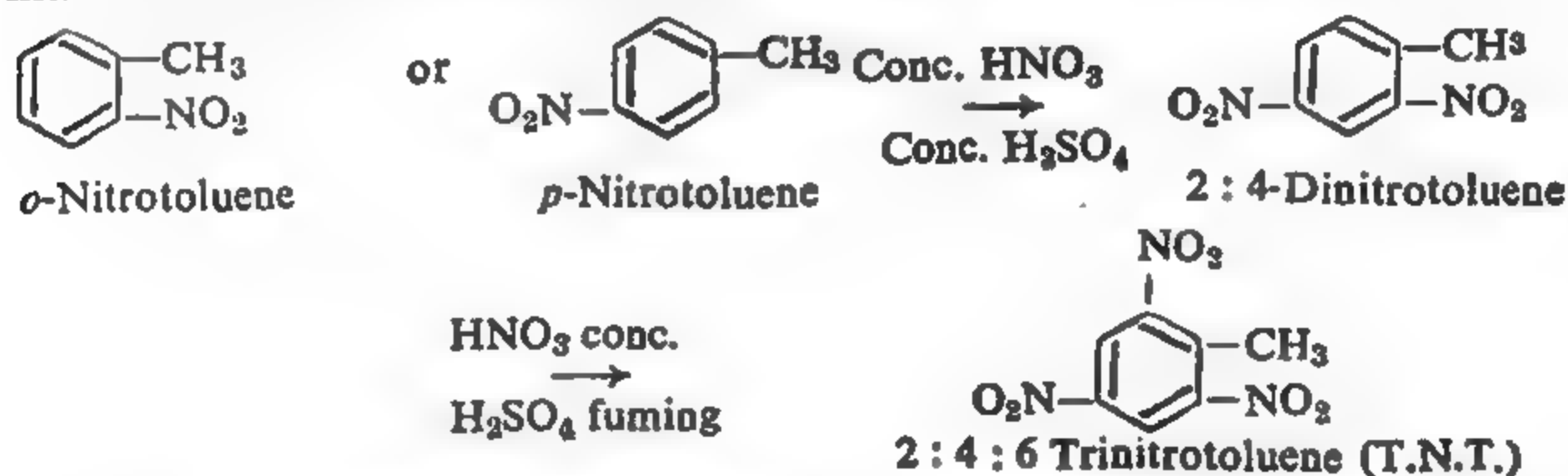


On a more drastic treatment, di- and tri-nitrobenzenes can be formed.

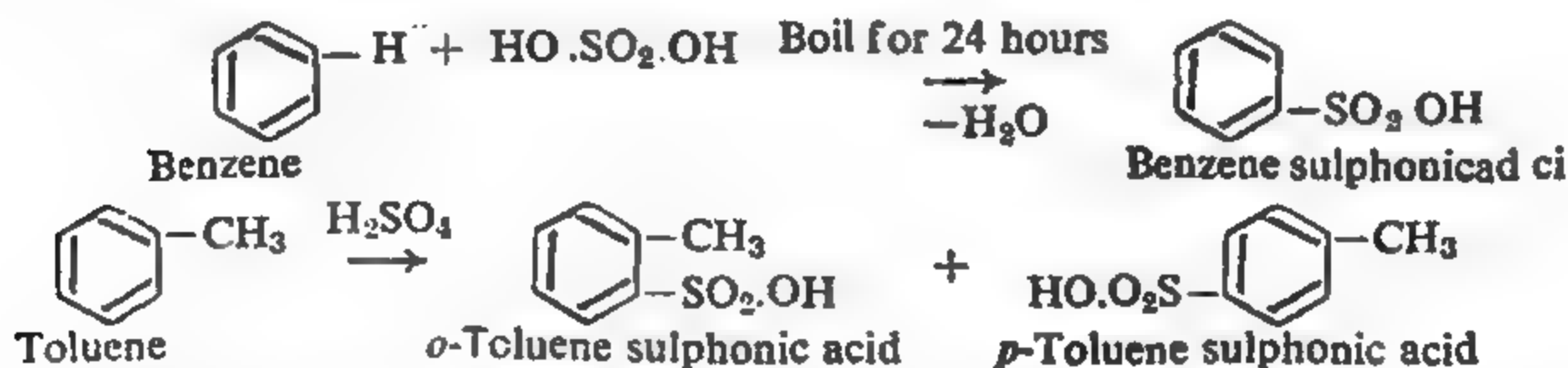
Toluene reacts as under :



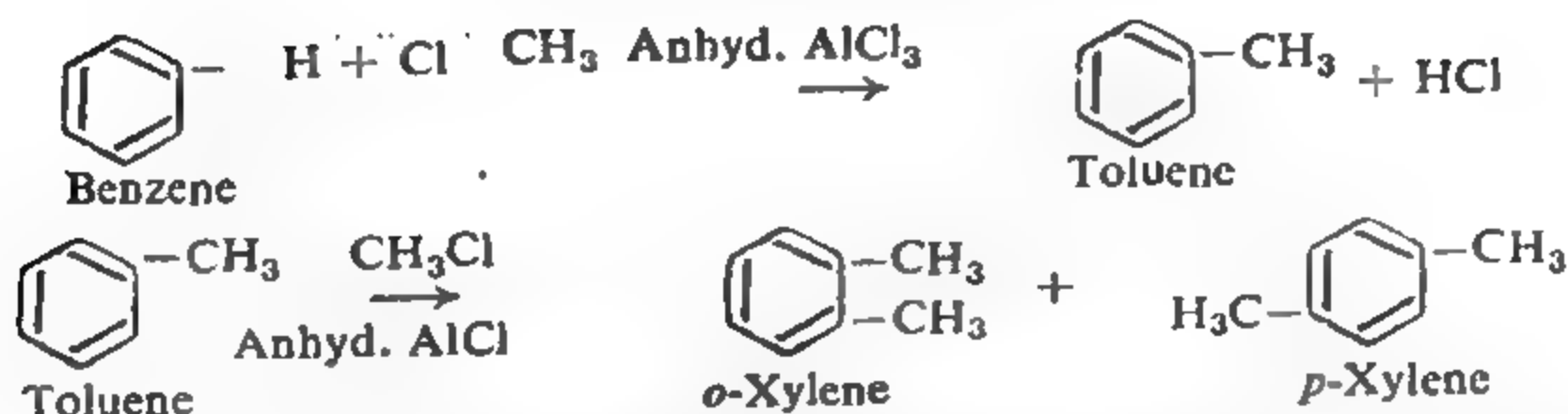
Treatment with excess of concentrated nitric acid results in the formation of di- and tri-nitrotoluene.



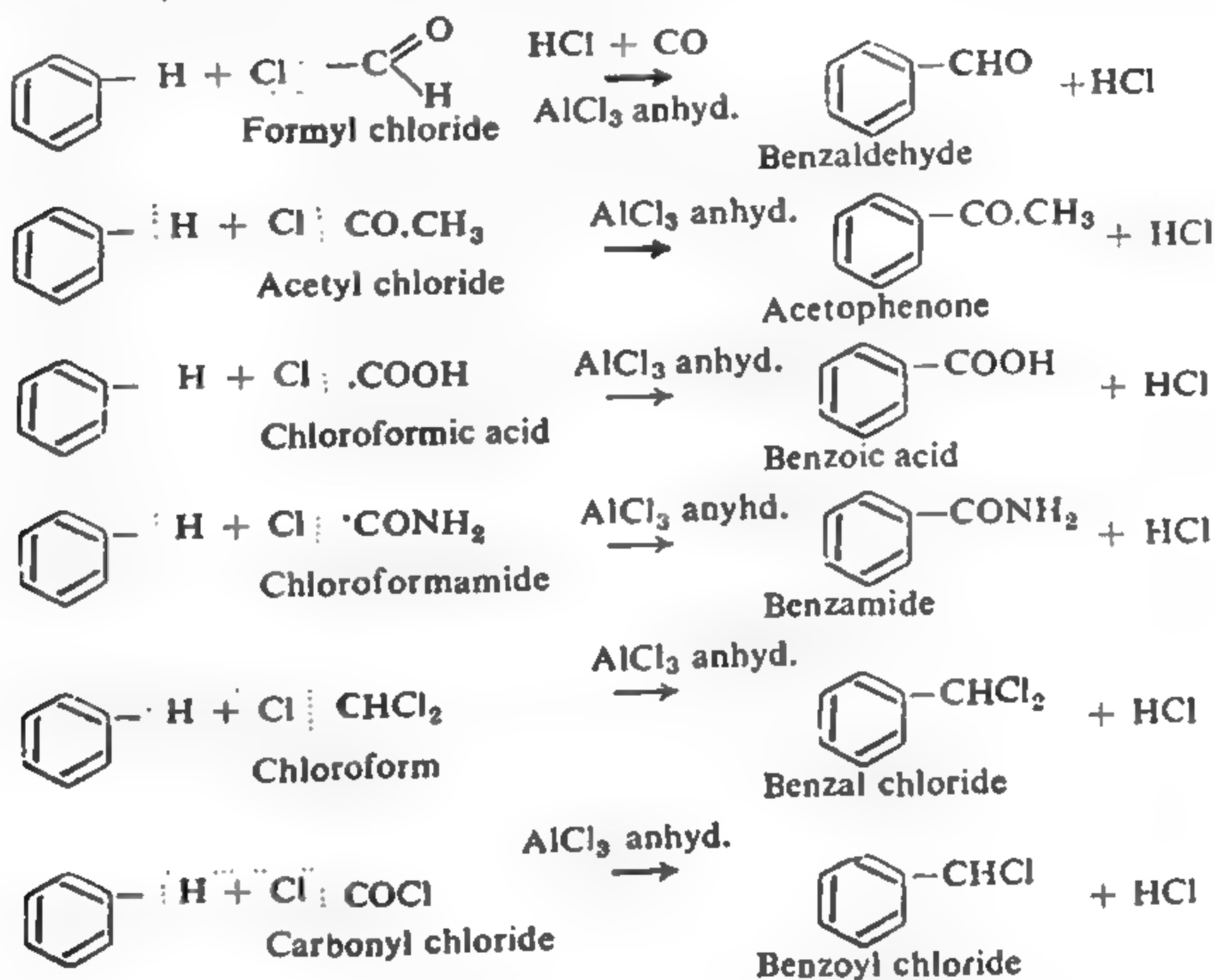
(3) **Sulphonation.** When boiled with concentrated sulphuric acid for a long time, one or more hydrogen atoms of the benzene nucleus are replaced by the sulphonic acid group ($-\text{SO}_2\text{OH}$). This process is known as *sulphonation*. For example,



(4) **Alkylation.** On treatment with alkyl halides in the presence of anhydrous aluminium chloride (**Friedel and Craft's reaction**), the hydrogen atoms of the nucleus are replaced by the alkyl radicals. This process is known as *alkylation*. For example,



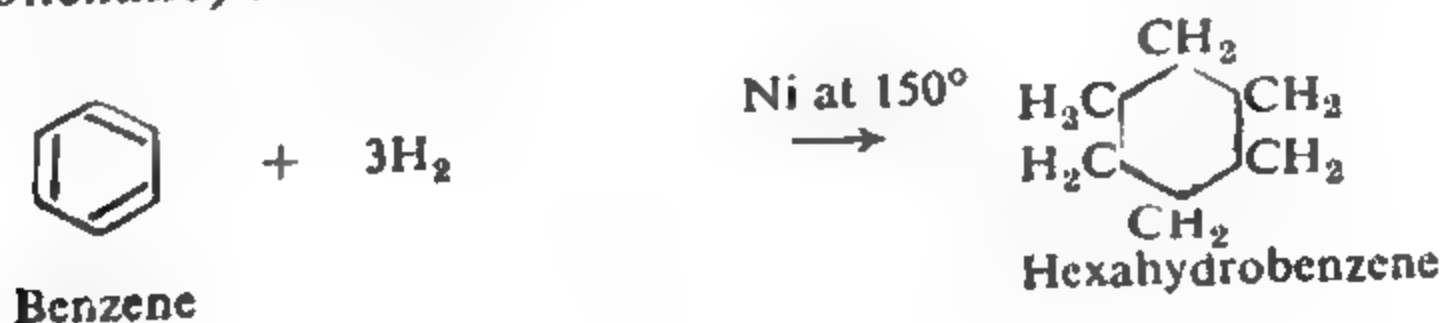
With the help of **Friedel and Craft's reaction**, benzene (or its homologues) can be converted *directly* into aldehydes, ketones, acids, amides, acid chlorides, and so on, as shown below :



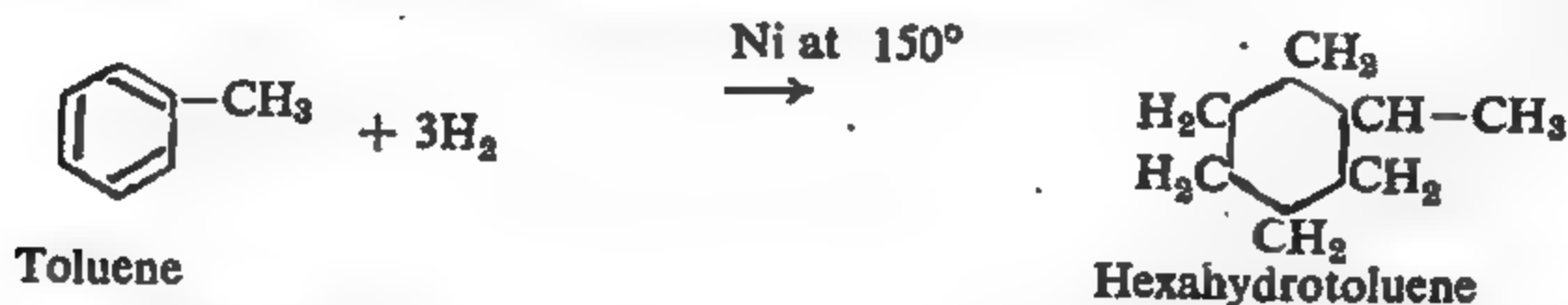
II. Addition Reactions.

Benzene and its homologues add up hydrogen and halogens (chlorine or bromine) to give corresponding addition products. Benzene adds up ozone giving benzene triozonide.

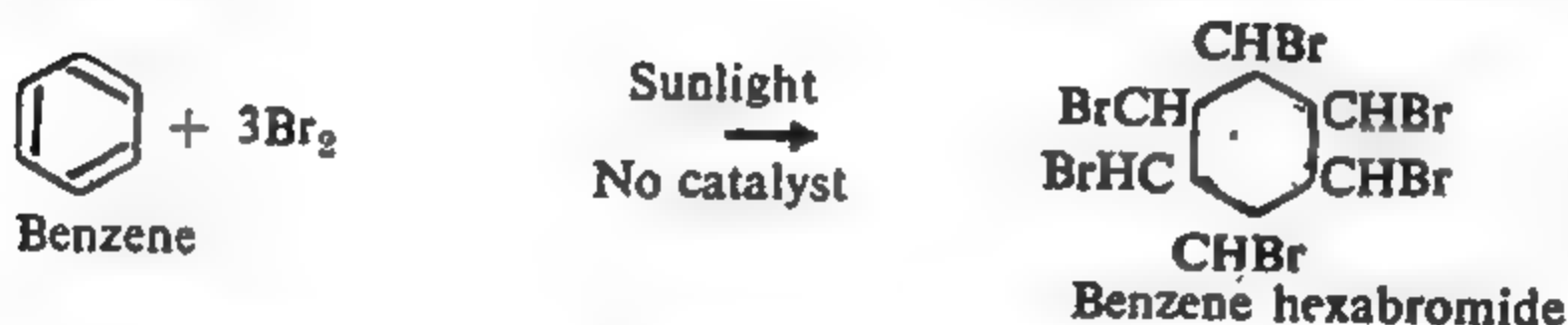
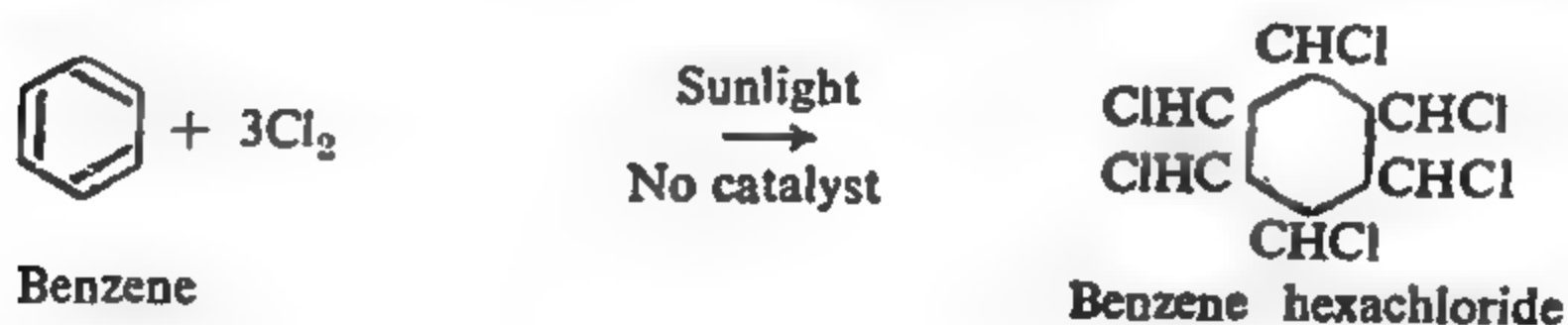
(1) **Addition of hydrogen.** If a mixture of benzene and hydrogen vapours is passed over finely divided nickel at 150° , hexahydro benzene (cyclohexane) is formed.



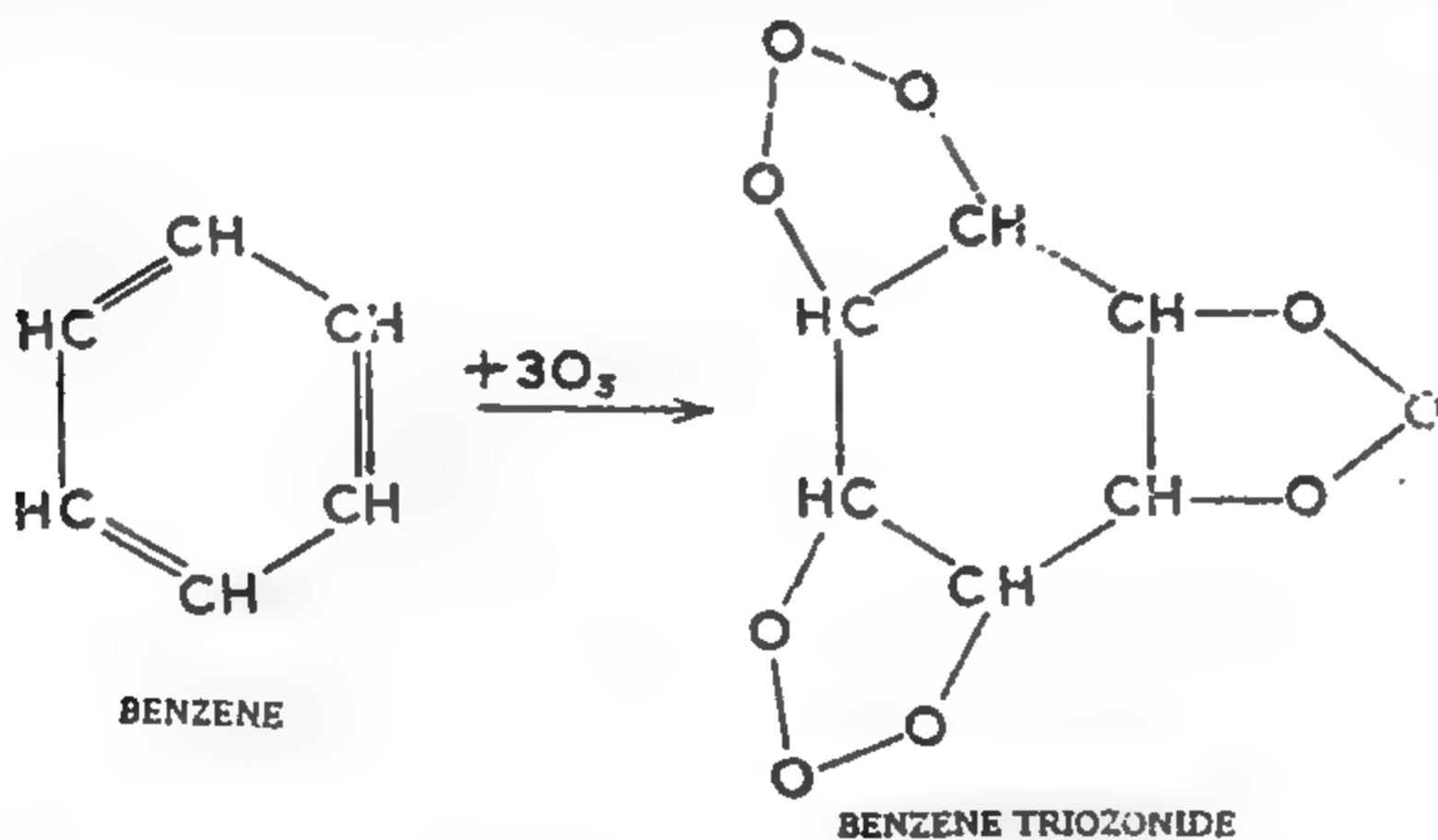
It is of interest to note that hexahydrobenzene (or cyclohexane) does not possess any of the aromatic properties.



(2) **Addition of halogens.** Benzene adds up chlorine and bromine in the *presence of direct sunlight and in the absence of a catalyst* to form ultimately *benzene hexachloride* and *benzene hexabromide* respectively.

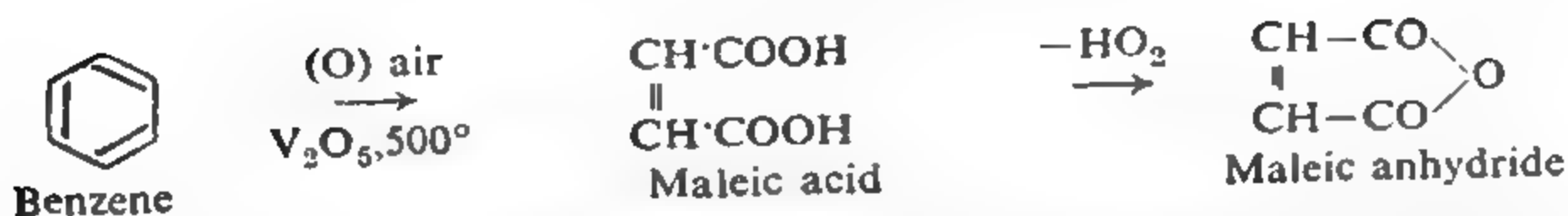


(3) **Addition of ozone.** Benzene adds up ozone forming benzene triozoneide.

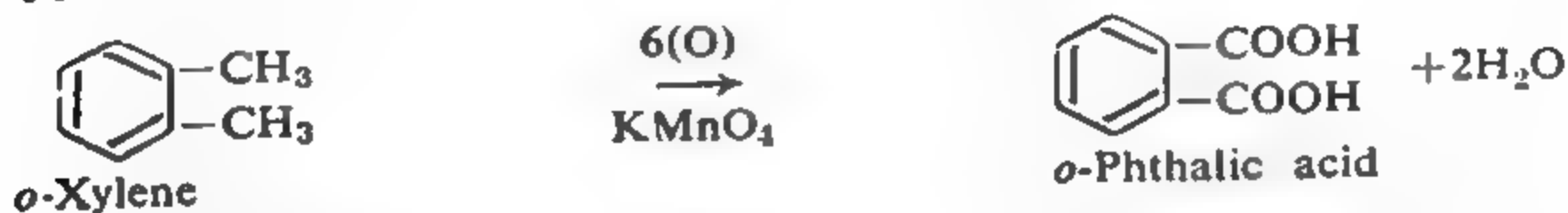
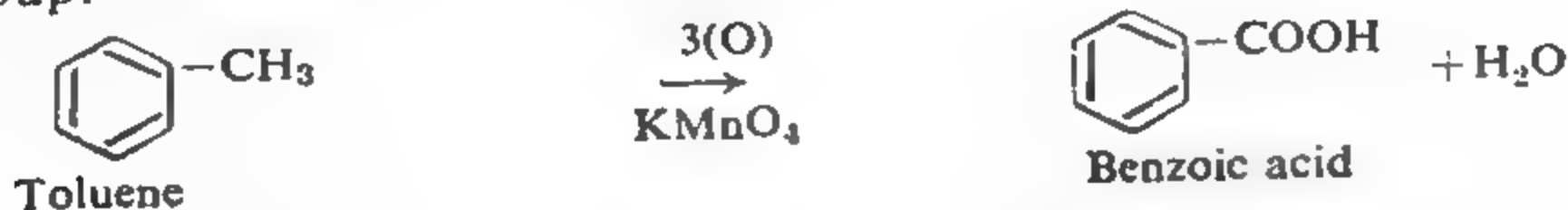


III. Oxidation

(i) Benzene is not attacked by oxidising agents like potassium permanganate and dichromate. However, *vapour phase oxidation* of benzene is quickly brought about by passing its vapour over vanadium pentoxide heated to 500° , in the presence of air, to yield maleic anhydride. Benzene ring gets ruptured in this case.

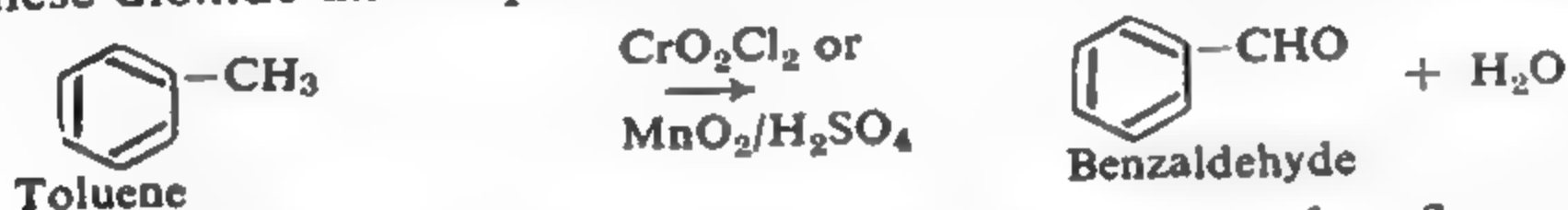


(i) Toluene and other homologues are readily attacked by potassium permanganate when the side chain is oxidised to carboxyl group.



It is of interest to note that the side chain, however long it may be, is oxidised by permanganate to a single carboxyl group.

With milder oxidising agents like chromyl chloride (CrO_2Cl_2), manganese dioxide and sulphuric acid, toluene is oxidised to benzaldehyde.



(iii) Aromatic hydrocarbons burn with a smoky flame, giving carbon dioxide and water.



INDIVIDUAL MEMBERS

BENZENE, C_6H_6

Benzene was obtained for the first time in 1825 by Faraday, who isolated it from an oil condensed in cylinders carrying compressed illuminating gas (coal gas). In 1833, Mitscherlich prepared benzene by the decarboxylation of benzoic acid obtained from 'gum benzoin' and hence its name. In 1845, Hofmann discovered benzene in coal tar which continues to be the richest source of benzene.

Methods of preparation. Benzene can be prepared from sodium benzoate, phenol, sulphonic acid, benzene diazonium chloride and Grignard reagents by the methods discussed earlier (cf. general methods of preparation).

Benzene can also be prepared by the polymerisation of acetylene by passing it through a red hot silica or copper tube.



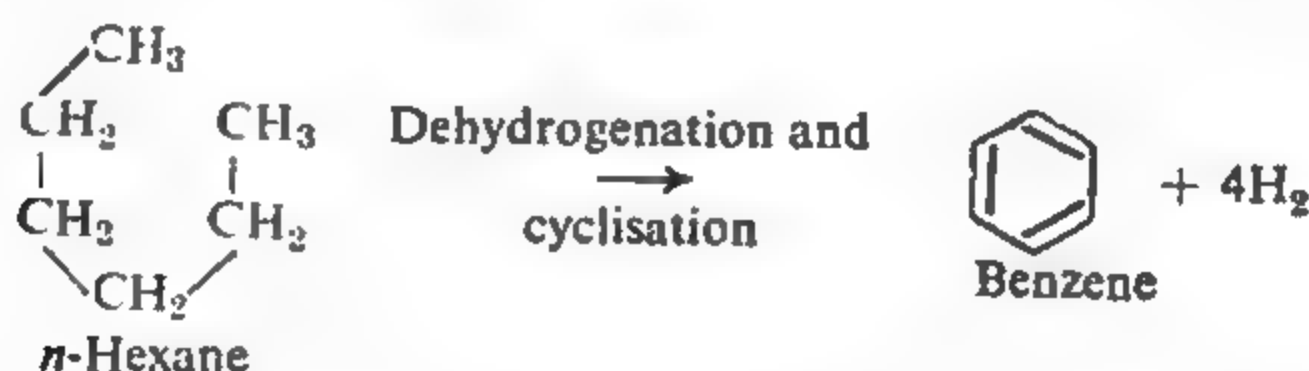
It is also obtained in quantitative yield when phenyl hydrazine is warmed with an aqueous solution of copper sulphate or ferric chloride.



Industrial Preparation. (1) **From coal tar.** The most important source of benzene is coal tar from which it is recovered as discussed earlier.

(2) **From coke-oven gas.** When coal is destructively distilled for the manufacture of coke, the coal gas obtained is very rich in aromatic hydrocarbons like benzene, toluene, xylene, etc. This gas is passed up a tower from the top of which creosote oil is sprayed. The aromatic hydrocarbons are dissolved by creosote oil from which they are recovered as *light oil* by steam distillation and are then separated by fractionation, as already described.

(3) **From petroleum.** The lower boiling fractions of petroleum distillation are subjected to a process known as '*hydroforming*' in which the vapours of the petroleum fractions are passed through a catalyst consisting of molybdenum or vanadium oxide supported on alumina at 500° and under 10–20 atmospheres pressure. Thus, the paraffin, *n*-hexane, present in petroleum, undergoes dehydrogenation and cyclisation to yield benzene.



Physical Properties. Benzene (m.p. 5.5° , b.p. 80.1°) is a colourless, inflammable liquid with a characteristic aromatic smell. It is insoluble in water but soluble in organic solvents. It is an excellent solvent for oils, fats, resins, sulphur, iodine, etc. Benzene is lighter than water (density = 0.899 at 0°).

Chemical Properties. Benzene is a stable compound and is not attacked by acids, alkalies, and oxidising agents. It, however, undergoes a variety of *substitution reactions* such as *nitration*, *sulphonation*, *halogenation* and *alkylation*. Under suitable conditions it also gives *addition reactions* with *hydrogen*, *halogens* and *ozone*. On drastic *oxidation* it yields maleic anhydride. All these properties have already been discussed in details (see general properties).

Uses. Benzene is used :

- (i) As a motor fuel along with petrol.
- (ii) As an excellent solvent for oils, fats, waxes, resins, iodine, sulphur, phosphorus. etc.
- (iii) In dry cleaning.
- (iv) As a raw material for the large scale production of many useful compounds such as nitrobenzene, aniline, benzaldehyde, phenol, *gammexane* (an efficient insecticide) and also in the preparation of dyes, drugs and explosives.

Constitution of Benzene.

(1) The qualitative and quantitative analyses show that the molecular formula of benzene is C_6H_6 .

(2) Benzene appears to be a highly unsaturated compound as the corresponding alkane would be hexane (C_6H_{14}). Keeping in view the tetravalency of carbon and monovalency of hydrogen, benzene could be represented by any one of the following open chain formulae :

- (I) $HC \equiv C - CH_2 - CH_2 - C \equiv CH$
- (II) $H_2C = CH - C \equiv C - CH = CH_2$
- (III) $H_3C - C \equiv C - C \equiv C - CH_3$

(3) But benzene does not show the characteristic reactions of compounds containing double or triple bonds as

- (i) it does not react with alkaline potassium permanganate (Baeyer's reagent).
- (ii) it fails to decolorise bromine water.
- (iii) it does not add up hydrogen halides or hypochlorous acid.
- (iv) it is not affected by cold concentrated sulphuric acid.

(4) At the same time, it does show some addition reactions, such as

- (i) catalytic addition of hydrogen to give a hexahydro-compound, C_6H_{12} .
- (ii) addition of halogens, at high temperature and in the presence of sunlight, to give hexa halogen derivatives.

(iii) addition of three molecules of ozone to form a triozone.

(5) The above facts taken together prove that although benzene contains unsaturation, yet this unsaturation is not of the type shown by ethylene or acetylene. Hence the problem is to indicate unsaturation of benzene, somehow, which should be different from that which occurs in aliphatic compounds.

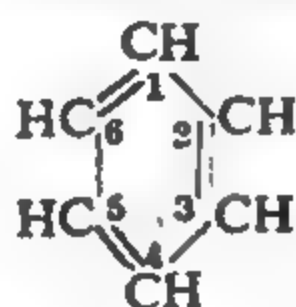
Along with this, there are two more facts which should be kept in view while assigning a structural formula to benzene, *viz.*,

- (i) Benzene forms *only one* monosubstitution product of the type C_6H_5X where X is a monovalent atom or group.

(ii) Benzene forms *three and only three* types of isomeric disubstitution products of the type $C_6H_4X_2$ or C_6H_4XY where X and Y are monovalent atoms or groups.

While the first fact points out that all the six hydrogen atoms of benzene are equivalent (*cf.* structure of methane), the second fact shows that the hydrogen atoms are occupying such positions that they *form three and only three different pairs*.

(6) Taking into consideration the above facts, Kekule, a German chemist, in 1865, suggested that benzene could be represented as a regular hexagon with a $-CH$ group present at each of its corners and to account for the tetravalency and monovalency of carbon and hydrogen respectively, he suggested the presence of alternate single and double bonds in its formula. Thus, benzene could be represented as

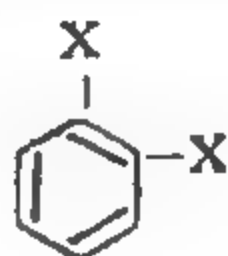


(7) This structure contains three double bonds and at once accounts for :

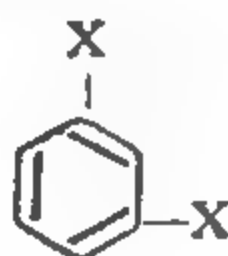
(i) The addition of three molecules of hydrogen, three molecules of chlorine and three molecules of ozone.

(ii) The formation of one and only one monosubstitution product of the type C_6H_5X . Since all the hydrogens are identical, any one of them can be replaced by the group X giving only one monosubstitution product.

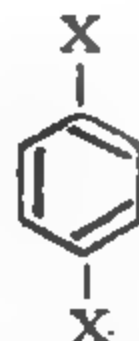
(iii) The formation of only three isomeric disubstitution derivatives of the type $C_6H_4X_2$ or C_6H_4XY . These will be 1 : 2, 1 : 3 and 1 : 4-disubstituted products as 1 : 5 and 1 : 6 disubstituted products will be equivalent to 1 : 3 and 1 : 2 compounds respectively. Thus, the three disubstituted derivatives would be



1 : 2 Disubstituted
derivative (*o*-)



1 : 3 Disubstituted
derivative (*m*-)



1 : 4 Disubstituted
derivative (*p*-)

(8) The above representation of benzene, however, suffered from two defects :

(i) There are three double bonds in the structure and hence benzene must be a highly unsaturated compound whereas, in actual practice, benzene behaves more like a saturated than an unsaturated compound. It gives substitution reactions more easily than the addition reactions.

(ii) There should be *two* 1 : 2 or *ortho*-disubstitution products according as the two substituents are present across a single bond or across a double bond as represented below :



But actually only one 1 : 2 disubstituted product is known.

(9) To meet with the above objections, Kekule (1872) suggested that :

(i) The double bonds, when present in a closed chain or ring compound, would behave differently than when present in an open chain compound, and

(ii) The formula of benzene is not a static but a dynamic one, that is, single and double bonds are continuously changing positions. Thus, the true representation of the benzene molecule will be

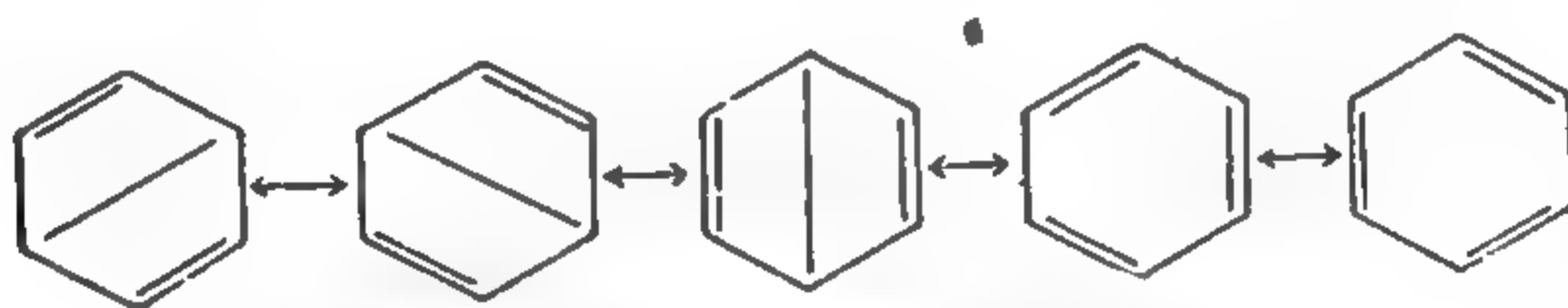


Obviously, the positions 1 : 2 and 1 : 6 will be identical.

(10) The equivalence of all the six carbon atoms in benzene is best represented at the present time by a hexagon containing a circle, *viz.*,



(11) The extraordinary stability of benzene is ascribed to the fact that benzene is a resonance* hybrid of various structures and is represented as below :



TOLUENE, METHYL BENZENE, $C_6H_5.CH_3$

Toluene occurs in a resin known as *tolu balsam* from which it is obtained by distillation. The chief source of toluene, however, is coal tar.

*Sometimes a compound is capable of being represented by two or more different structures (as in case of benzene) such that these structures differ from each other only in respect of the distribution of electrons, the position of various atoms remaining identical in all these structures. Such a compound is said to be a *resonance hybrid* of all these structures, which are called *resonating forms*, and it is always more stable than could be expected from any of its resonating forms. A detailed discussion of the formation of resonance hybrids is, however, beyond the scope of the book.

SUMMARY OF TYPICAL MEMBERS

PREPARATION AND PROPERTIES OF BENZENE

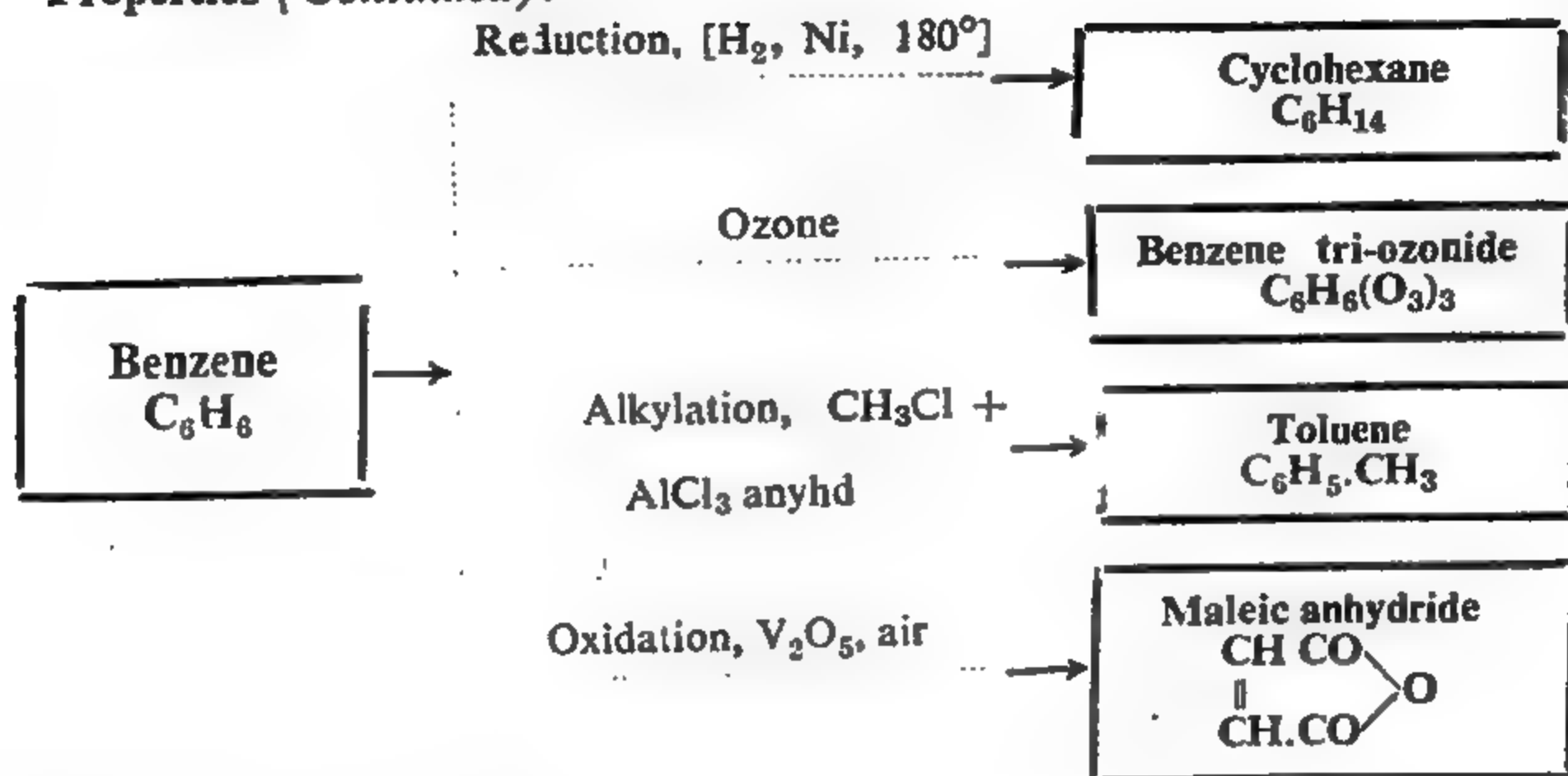
Preparation.

Acetylene $\text{HC}\equiv\text{CH}$	Polymerisation (Red hot tube) →	
Phenol $\text{C}_6\text{H}_5\text{OH}$	Distil with zinc dust →	
Sod. benzoate $\text{C}_6\text{H}_5\text{COONa}$	Distil with soda lime →	
Ben. diazonium chloride $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{Cl}$	Reduction with $\text{SnCl}_2 + \text{NaOH}$ →	Benzene C_6H_6
Benzene sulphonic acid $\text{C}_6\text{H}_5\text{SO}_2\text{OH}$	Hydrolysis with superheated steam →	
Phenyl hydrazine $\text{C}_6\text{H}_5\text{NH.NH}_2$	$\text{CuSO}_4 + \text{H}_2\text{O}$ or FeCl_3 →	
Petroleum n-Hexane	Catalytic dehydrogenation and cyclisation →	
Light oil	Fractional distillation through 90% benzol →	

Properties.

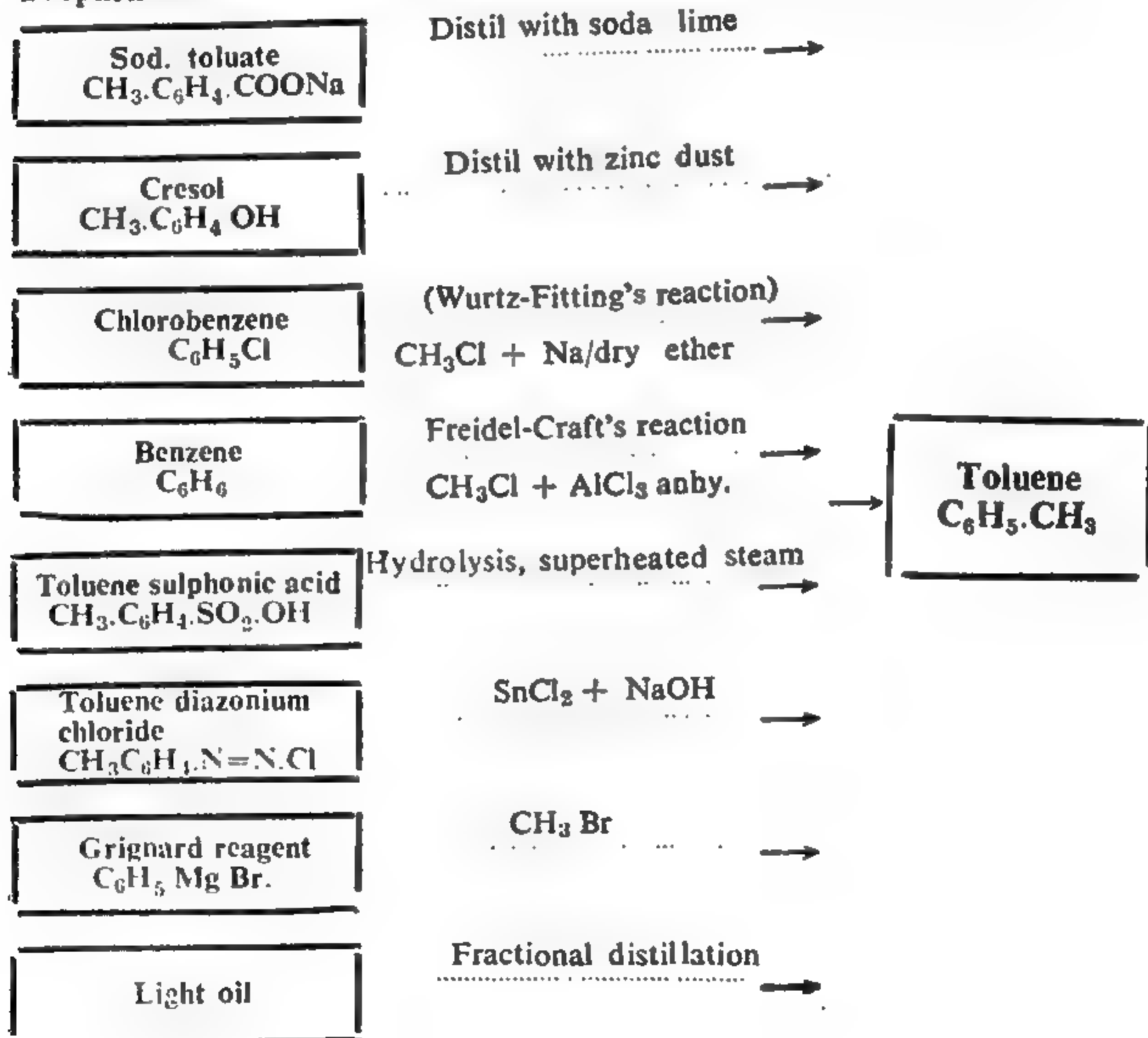
Benzene C_6H_6	Halogenation, Cl_2 , room temp. catalyst, diffused sunlight →	Chlorobenzene $\text{C}_6\text{H}_5\text{Cl}$
	Halogenation, Cl_2 no catalyst, direct sunlight →	Benzene hexa-chloride $\text{C}_6\text{H}_6\text{Cl}_6$
	Sulphonation, H_2SO_4 , 80° →	Benzene sulphonic acid $\text{C}_6\text{H}_5\text{SO}_2\text{OH}$
	Nitration 60° , $\text{HNO}_3 + \text{H}_2\text{SO}_4$ →	Nitrobenzene $\text{C}_6\text{H}_5\text{NO}_2$

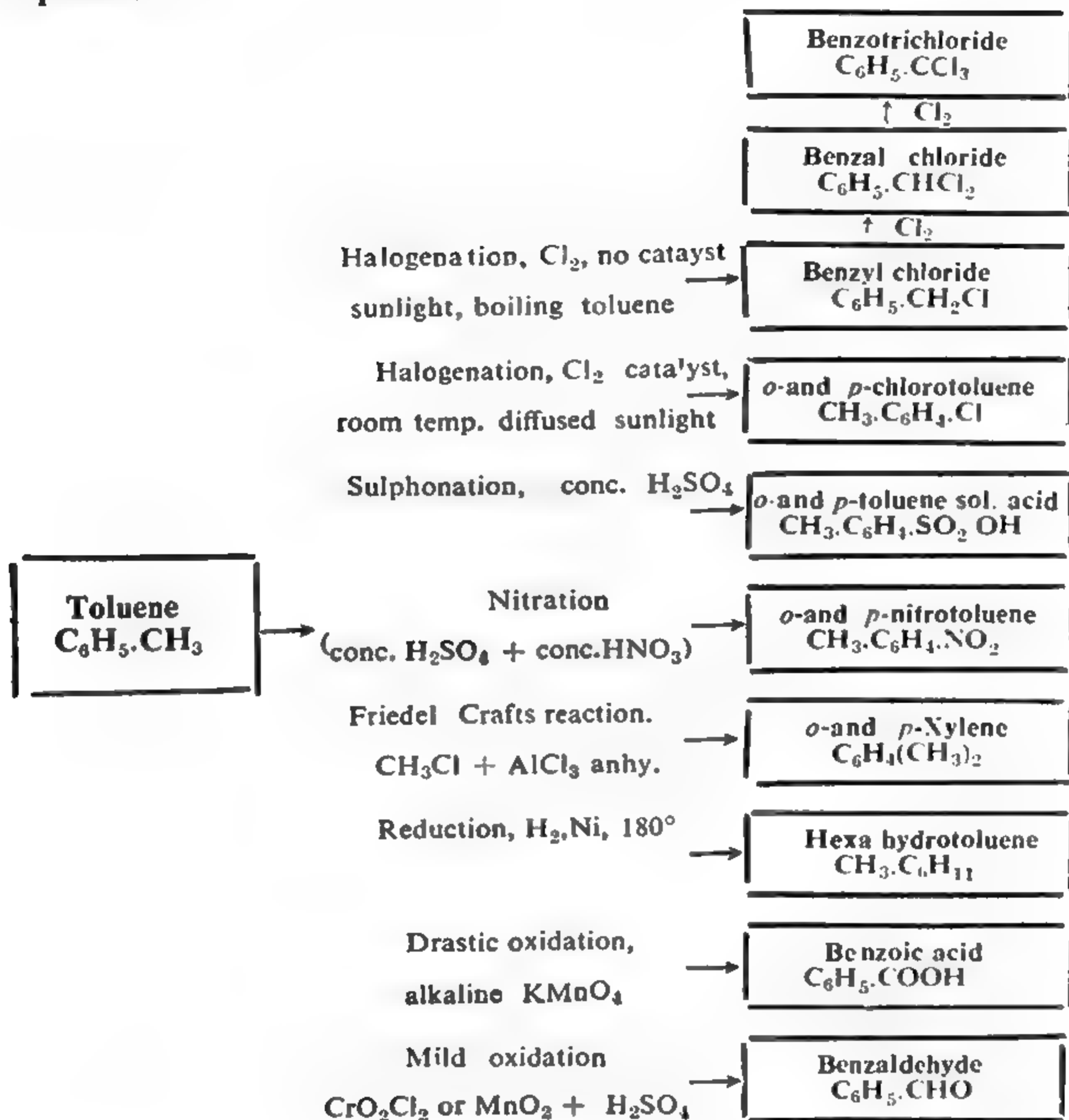
Properties (Continued).



PREPARATION AND PROPERTIES OF TOLUENE

Preparation.



Properties.

QUESTIONS

- Describe the general methods of preparation of aromatic hydrocarbons. In what ways do these hydrocarbons differ from aliphatic hydrocarbons?
- Discuss the methods of preparation of benzene. What are its important properties?
- How is benzene obtained on a commercial scale? How does it react with (i) chlorine (ii) sulphuric acid (iii) nitric acid (iv) methyl chloride in the presence of anhydrous aluminium chloride and (v) ozone?
- Write short notes on: (a) Friedel and Craft's reaction (b) Fittig's synthesis (c) Oxidation of benzene homologues (d) Chlorination of toluene.
- Discuss the evidence upon which the ring structure of benzene is based.

6. Give the methods of preparation of toluene. Compare and contrast the properties of benzene and toluene. How would you convert benzene into toluene and vice versa ?

7. (a) What is benzene ? Discuss its constitution. *(Panjab Inter 1961 S)*

(b) Deduce the structural formula of benzene. *(Panjab Inter 1960 S)*

8. Explain the meaning of "Substitution and sulphonation" in aromatic organic chemistry. Give one example of each, stating the conditions under which the reactions occur. *(Panjab 1957 S)*

9. Describe the commercial preparation of thiophene-free benzene. How does it react on exhaustive nitration and sulphonation ? Mention briefly the salient points which help in deducing the constitution of the hydrocarbon.

10. What do you understand by the term "Ring" and "Chain" substitution ? Illustrate your answer with examples. *(Panjab Inter 1952)*

11. "Though formula of benzene shows that it is unsaturated, it is almost as inert as saturated aliphatic hydrocarbons". Comment Give the structural formula of benzene. What would have been the formula had it been really completely saturated ? Discuss the probable reason for its special behaviour and unusual stability.

12. How is benzene prepared on a large scale ? Describe its properties and uses. Give its structural formula.

13. Explain giving equations, wherever possible, what happens when

(i) Concentrated nitric acid acts upon toluene,
(ii) Chlorine is passed into boiling benzene ? *(Panjab Inter 1963, 1964)*

14. What do you understand by (i) sulphonation (ii) nitration (iii) benzylation. *(Panjab Inter 1962)*

15. How can you cause in two different ways, the interconversion of benzene and toluene ? What happens when chlorine is passed through (a) boiling toluene in the absence of halogen carrier (b) cold toluene in the presence of a halogen carrier ?

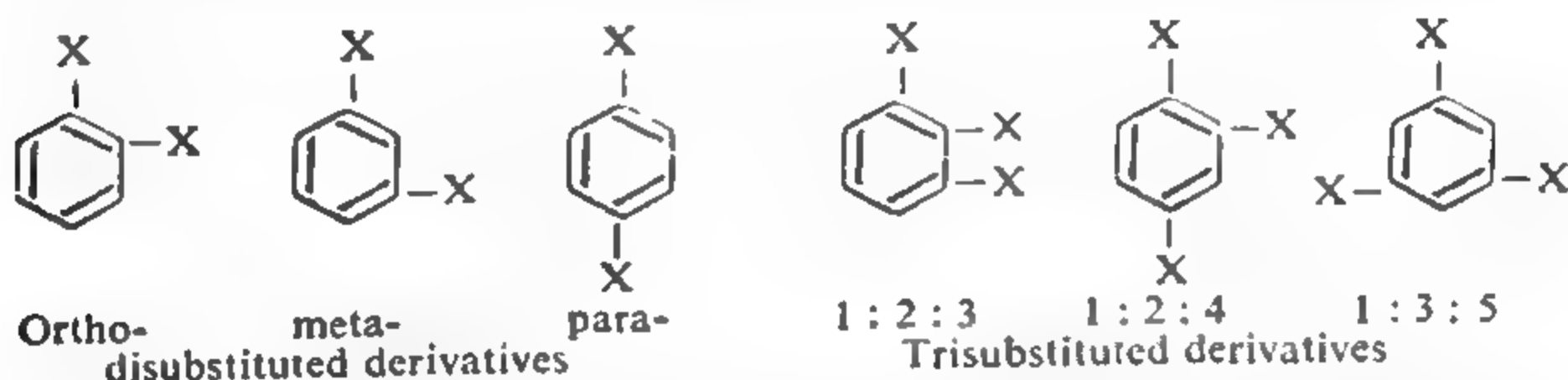
How do products of (a) contrast with those of (b) ? *(Panjab Inter 1960)*

16. Describe the preparation of toluene from 50% benzol. How can the hydrocarbon be converted into (a) benzyl alcohol (b) benzaldehyde (c) benzoic acid and (d) chlorotoluene ? *(Panjab Inter 1949)*

CHAPTER XLV

ORIENTATION OF BENZENE DERIVATIVES

As discussed in the previous chapters, benzene gives three disubstituted and three trisubstituted derivatives represented as below :



It is important to note that three trisubstitution products will be obtained only if three substituted groups are the same. If it is not so, the number of trisubstitution products will be much greater. For instance, if all the three substituents are different, ten isomers are possible and if one is different from the remaining two, six isomeric trisubstitution products are possible.

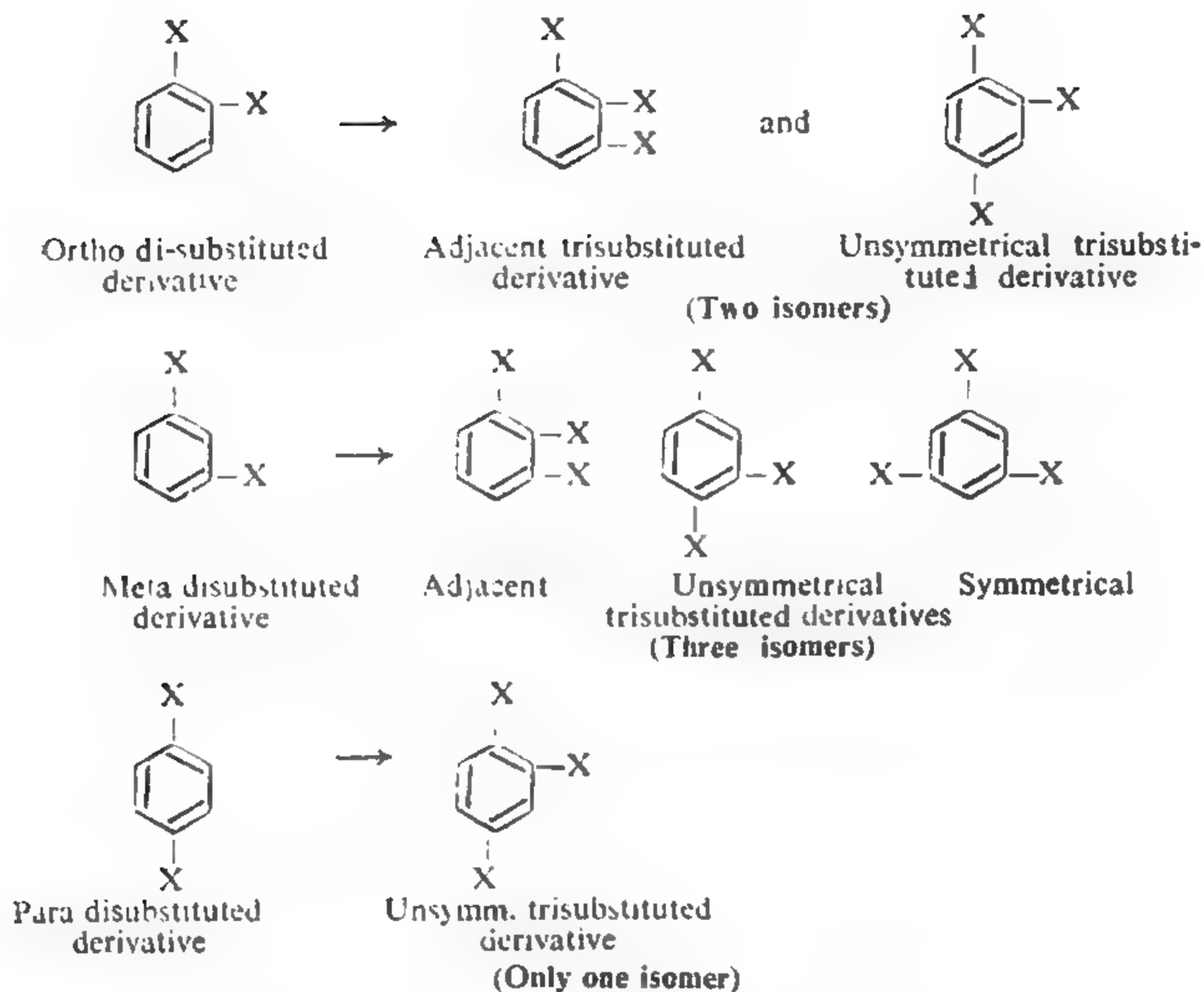
ORIENTATION

Suppose that a sample of xylene is given and it is required to know whether it is an ortho, meta or para compound. *This process of determining the relative positions of substituents in the benzene nucleus is called orientation.* Two methods for this purpose are available :

(1) *Korner's Absolute Method* (2) *Relative Method.*

(1) **Korner's Absolute Method.** (1874). This method consists in converting the given disubstituted compound into trisubstituted products and then determining the number of isomers obtained. The number of isomeric trisubstitution products obtained will decide whether the given disubstituted compound is ortho, meta or para.

It will be clear from the following that an *ortho* di-derivative would give two, the *meta* derivative three and a *para* derivative only one trisubstitution product.



Thus, the two steps in the Korner's absolute method are :

(a) To convert the given disubstituted compound, $C_6H_4X_2$, into the trisubstituted compound, $C_6H_3X_3$.

(b) To determine the number of isomers of $C_6H_3X_3$ formed., by fractional distillation or fractional crystallisation, etc.

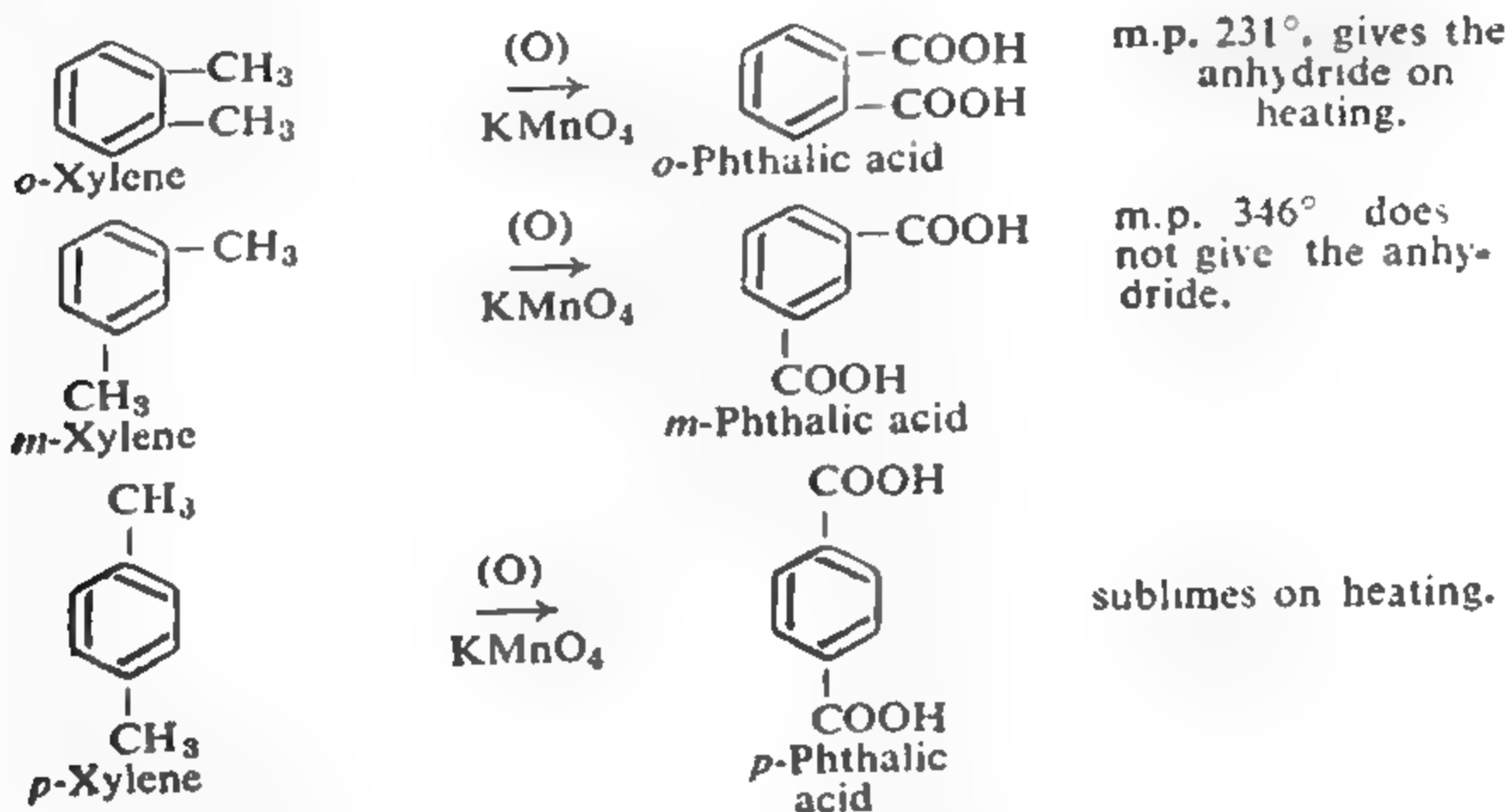
Obviously if $C_6H_3X_3$ is a *single* compound the given compound $C_6H_4X_2$ is *para*; if $C_6H_3X_3$ is found to exist in *two* isomeric forms, the given compound $C_6H_4X_2$ is *ortho* and if $C_6H_3X_3$ exists in *three* isomeric forms, then the given compound, $C_6H_4X_2$ is *meta*.

Limitation of Korner's method. This method, as would be clear, is theoretically an ideal one, that is, it would never fail. But, in actual practice it suffers from one defect, that is, that quite often the quantities of the trisubstituted derivatives obtained are too small to be resolved into the various isomers and hence the inference may be wrong.

Relative method. In this method, the compound whose orientation is required, is either produced from or is converted into another compound, the relative positions of substituents in which are already known. Assuming that during this conversion, the substituents do not change their relative positions, the orientation of the given compound can be easily established. For instance, the relative positions of the two methyl groups in a given sample of xylene can be determined by converting it into phthalic acid. For this purpose, the given sample

of xylene is treated with alkaline potassium permanganate when the two methyl groups get oxidised to the carboxyl groups and phthalic acid is obtained.

If the phthalic acid obtained melts at 231° and gives the anhydride easily, it is ortho-phthalic acid and the xylene from which it is obtained is also ortho. If the phthalic acid formed melts at 346° and does not form the anhydride, it is meta phthalic acid and the xylene from which it is obtained is also meta. Likewise, if the phthalic acid obtained simply sublimes on heating, it is paraphthalic acid and the parent xylene is also para.



This method is of a limited application only.

DIRECTIVE INFLUENCE OF GROUPS

Experience has shown that the groups already present in the benzene nucleus influence the positions taken up by the new entrants. For instance,

(a) There is certain category of groups like nitro ($-\text{NO}_2$), cyano ($-\text{CN}$), aldehydic ($-\text{CHO}$), etc., which have a meta directing influence on the new entrants.

(b) There is another class of groups, like hydroxyl ($-\text{OH}$), methyl ($-\text{CH}_3$), halogen atoms ($-\text{Cl}$, $-\text{Br}$, $-\text{I}$) etc., which exert an ortho and para directing influence on the new substituents.

This influence of groups (already present in the benzene nucleus upon the position to be taken up by the new entrants is called the directive or orienting influence.

There are certain empirical rules with the help of which the positions to be taken up by the new entrants can be predicted. One such rule is **Crum Brown and Gibson's Rule (1892)** which may be stated as follows :

A Group X, already present in the benzene nucleus, will be meta directing if its hydrogen compound HX, can be directly and readily oxidised to a stable compound HXO, otherwise X will be an ortho and para directing group.

The directive influence of groups is given in Table 1.

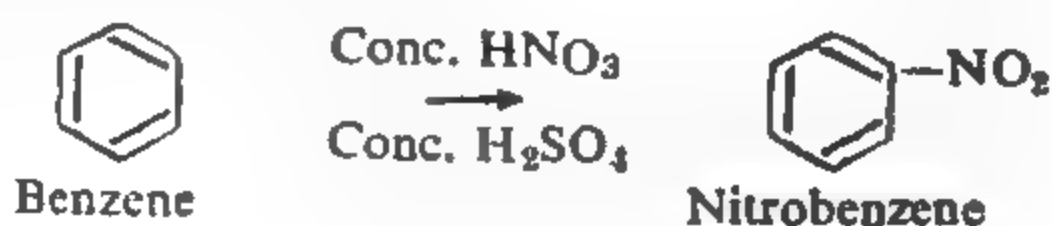
TABLE 1

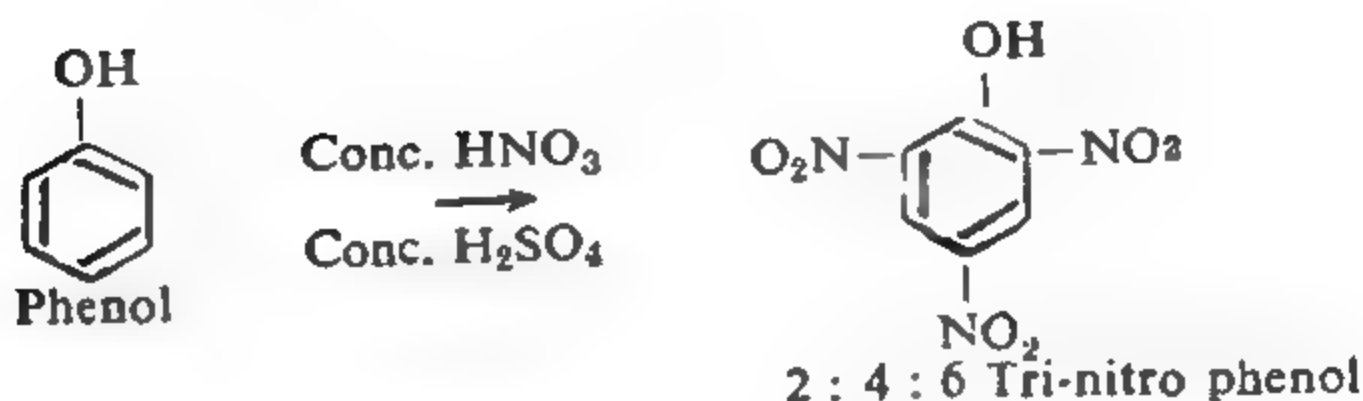
The Directive Influence of Various Groups

Group X	Hydrogen compound HX	Can HX be directly and readily oxidised to HXO ?	Directive influence
-NO ₂	HNO ₂	Yes to HNO ₃	Meta directing
-OH	H ₂ O	No	O—and <i>p</i> -directing
-NH ₂	NH ₃	No	O—and <i>p</i> -directing
-CH ₃	CH ₄	No	O—and <i>p</i> -directing
-Cl	HCl	No	O—and <i>p</i> -directing
-Br	HBr	No	O—and <i>p</i> -directing
-CHO	H.CHO	Yes to H.COOH	Meta directing
-COOH	H.COOH	Yes to CO ₂ +H ₂ O	Meta directing
-CN	HCN	Yes to HCNO	Meta directing
-SO ₂ .OH	H ₂ SO ₃	Yes to H ₂ SO ₄	Meta directing
-CONH ₂	H.CONH ₂	No	O—and <i>p</i> -directing
-CH ₂ Cl	CH ₃ Cl	No	O—and <i>p</i> -directing
-COCH ₃	CH ₃ .CHO	Yes to CH ₃ COOH	Meta directing

It must be fully understood that the *new entrant* has no directive influence whatsoever. The directive influence is of the group already present.

Experience has also shown that the groups already present in the nucleus not only influence the positions taken up by the new entrants but also the ease of substitution. As a rule, the ortho and para directing groups facilitate further substitution, while meta directing groups retard further substitution. For instance, a mixture of concentrated nitric acid and sulphuric acid, introduces only one nitro group in benzene but three nitro groups in phenol or toluene.





QUESTIONS

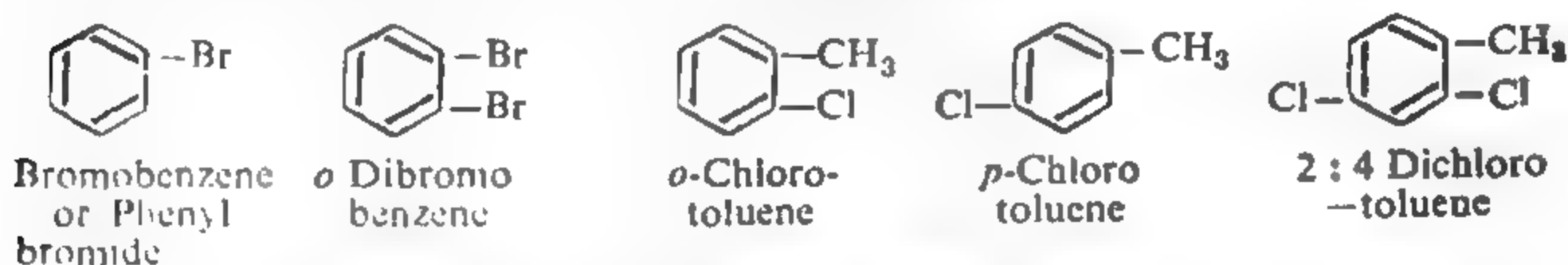
1. What do you understand by the term orientation? Discuss the methods of orientation available. How would you proceed to effect the orientation of dibromobenzenes?
2. There isomeric chlorotoluenes are known. How would you proceed to determine the position of chlorine atom with respect to the methyl group in each case?
3. What is meant by orientation? How would you establish whether a given sample of xylene is ortho, meta or para?
4. Write short notes on :
 (i) Korner's absolute method. (ii) Relative method for orientation.
5. What is meant by the directive influence of a group? How would you predict the position of new entrants if the benzene nucleus already contains (i) a hydroxyl group (ii) an aldehydic group?
6. Define Orientation and Crum Brown and Gibson's Rule. (Panjab Inter 1960 S)
7. Explain as clearly as possible with the help of examples (1) Crum Brown's Rule (2) Korner's Absolute method of orientation. (Panjab Inter 1958)
8. How many isomers are possible in case of :
 (i) Monosubstituted Benzene (ii) Disubstituted Benzene? Give reasons for your answer in the two cases
 In each case how would you establish the nature of different isomers, if any? (Panjab Inter 1953)
9. State Crum Brown and Gibson's Rule. Give its applications. Illustrate with the help of graphic formulae the products of reactions expected to result from :
 (i) Sulphonation of nitrobenzene (ii) nitration of phenol (iii) chlorination of nitrobenzene (iv) bromination of benzoic acid. (Panjab Inter 1952 S)
10. A compound of the formula $\text{C}_6\text{H}_4\text{Cl}_2$ is given to you. How would you proceed to orientate chlorine atoms in the compound? (Panjab Inter 1951)
11. State Crum Brown and Gibson's Rule. How does this rule help an investigator in locating the position of nitro group in the nucleus when the group is introduced in (i) benzaldehyde (ii) toluene (iii) phenol (iv) benzene sulphonic acid (v) benzyl chloride and (vi) nitrobenzene. (Panjab Inter 1950, 62)

CHAPTER XLVI

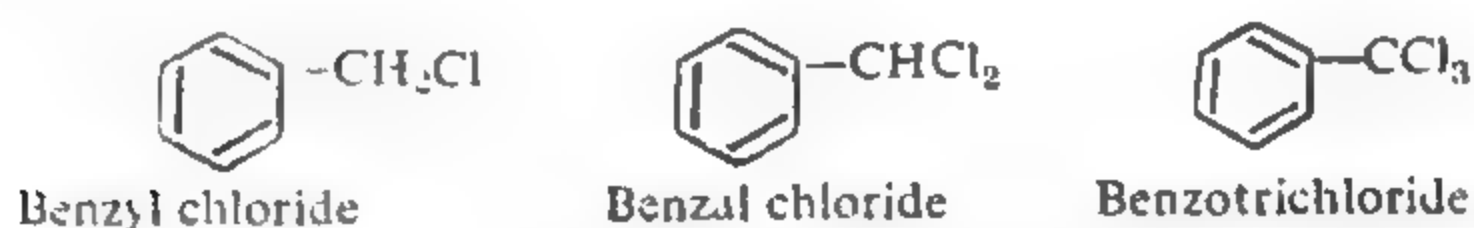
AROMATIC HALOGEN COMPOUNDS

The halogen substituted derivatives of aromatic hydrocarbons are of two types :

(a) **Nuclear Substituted Compounds.** Such compounds are formed by the replacement of one or more hydrogen atoms of the aromatic nucleus by halogen atoms. For example,



(b) **Side-Chain Substituted Compounds.** These compounds are obtained by the replacement of the hydrogen atoms of the side chain by the halogen atoms. Toluene, for instance, gives



In the nuclear substituted compounds, the halogen atoms are firmly attached to the benzene nucleus and cannot be easily replaced. However, when the aromatic nucleus contains two or more halogen atoms one of the halogen atoms can undergo replacement reactions more easily. The compounds with halogen atoms in the side chain are as reactive as the alkyl halides and undergo all the substitution reactions of the alkyl halides.

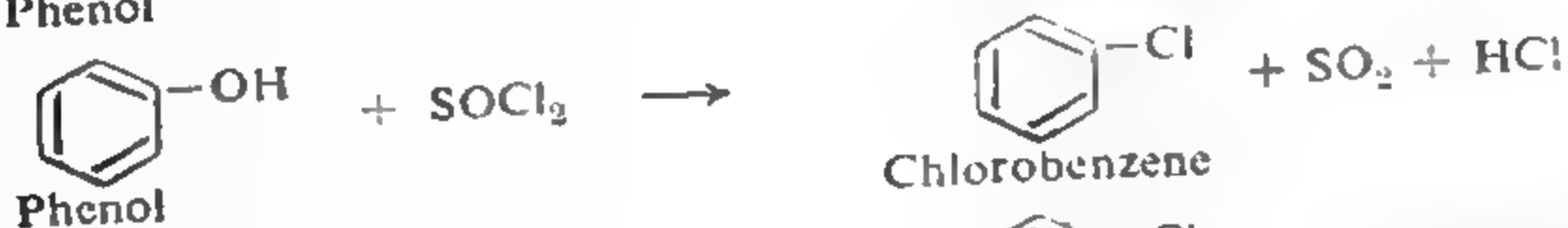
General Methods of Preparation

(A) For Nuclear Substituted Compounds.

The following methods are available for the preparation of nuclear substituted halogen compounds :

(1) **Direct halogenation.** Benzene and other aromatic hydrocarbons react with chlorine and bromine in the presence of halogen carriers, yielding nuclear substituted derivatives. Iodine also reacts but in the presence of an oxidising agent. (See general properties of aromatic hydrocarbons).

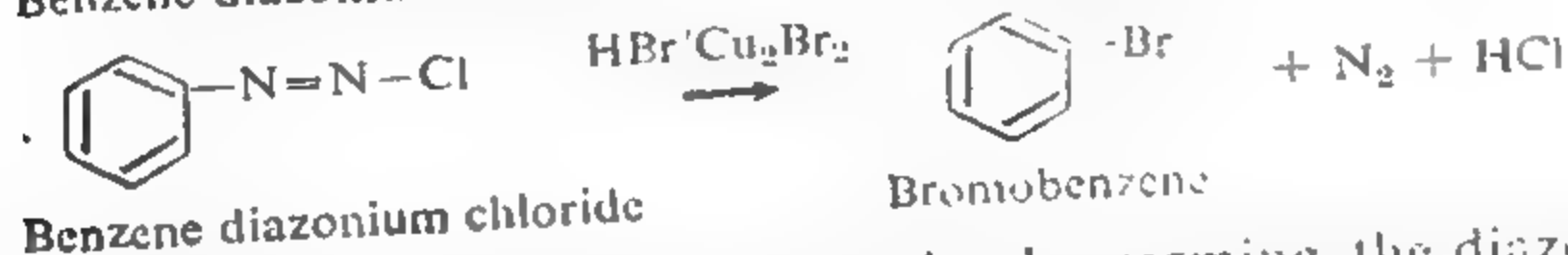
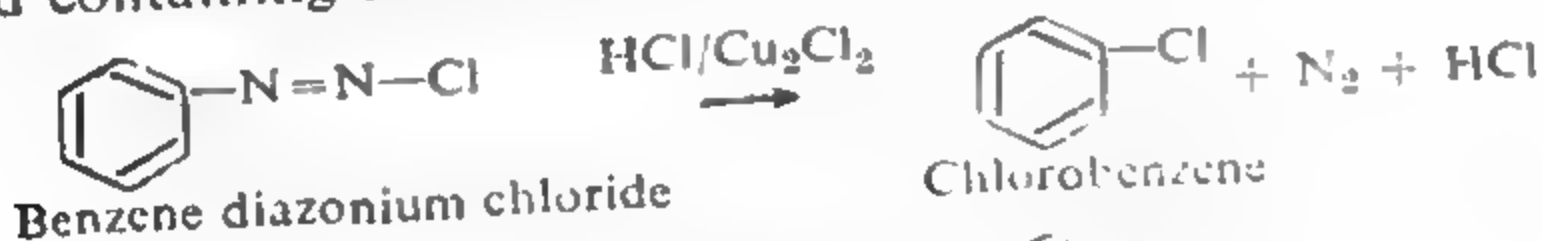
(2) **Action of phosphorus pentachloride or thionyl chloride on phenols.**



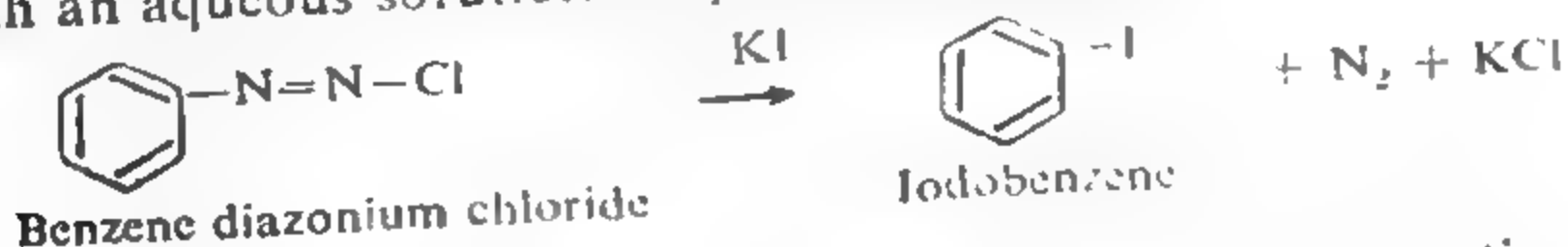
(3) **Action of hypobromous acid on the corresponding hydrocarbon.**



(4) **Sandmeyer's reaction.** This is the most convenient method for the preparation of chloro- and bromo- derivatives. The method consists in pouring the diazonium salt solution into hydrochloric or hydrobromic acid containing the corresponding cuprous salt (catalyst). For example,



Iodo-benzene can be obtained by simply warming the diazonium salt with an aqueous solution of potassium iodide.



This is the best available method for the preparation of iodo-derivatives.

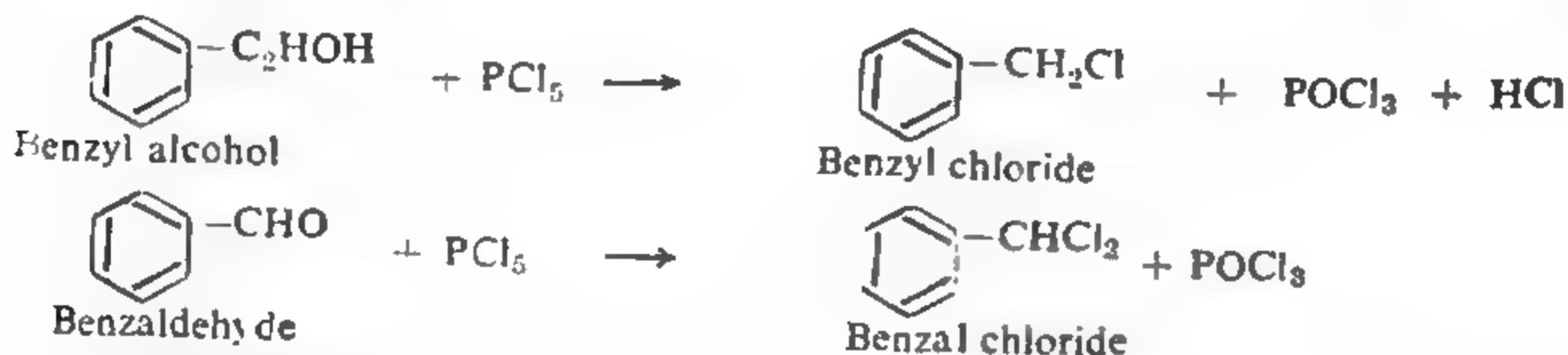
(5) **Gatterman's reaction.** This is simply a modification of Sandmeyer's reaction with the difference that the cuprous salts are replaced by copper powder.

(B) For Side-Chain Derivatives.

The following methods can be used for the preparation of side-chain substituted halogen compounds :

(1) **Direct halogenation of toluene.** (See general properties of aromatic hydrocarbons).

(2) **Action of phosphorus pentachloride or thionyl chloride on aromatic alcohols or aldehydes.**

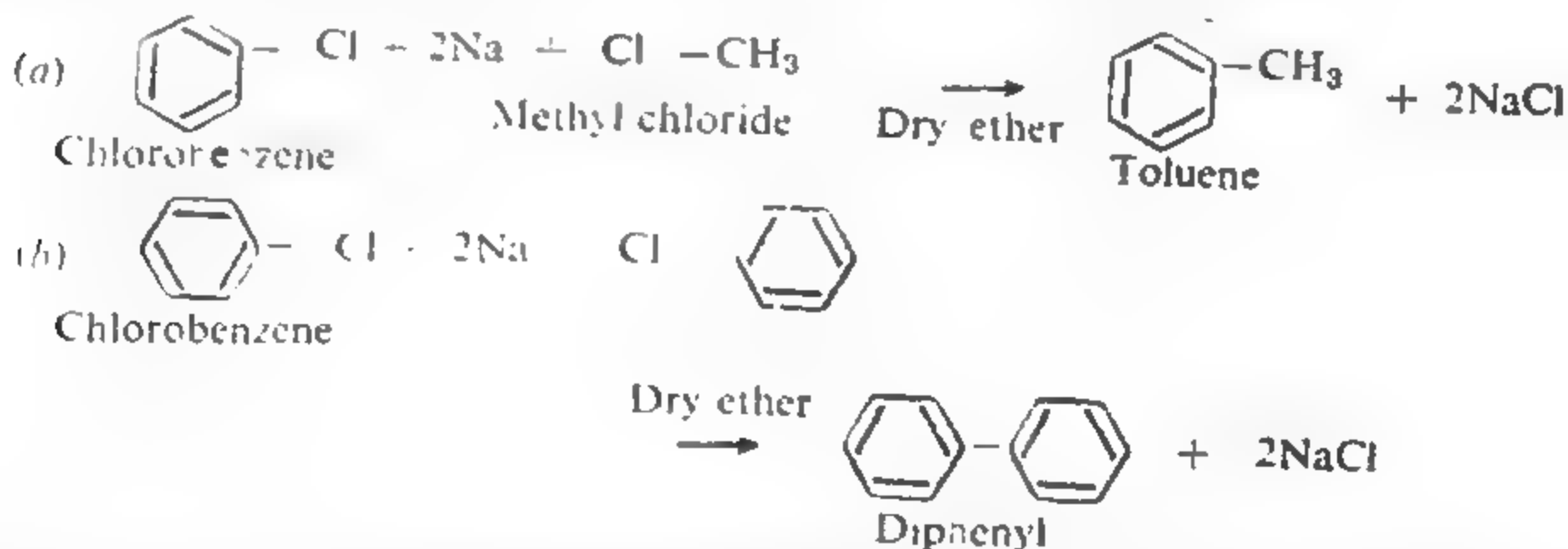


Physical Properties. The nuclear substituted derivatives are colourless liquids or solids with a pleasant odour while the side chain compounds have an irritating smell. They are insoluble in water but soluble in organic solvents.

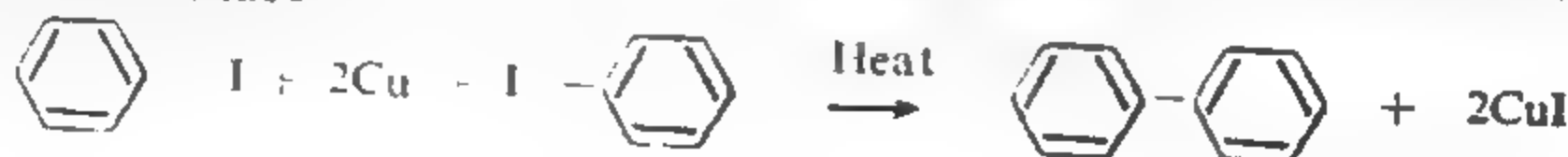
Chemical Properties.**(A) Of Nuclear Substituted Halogen Compounds.**

(a) **Reactions of the Halogen Atom.** As stated earlier, the halogen attached to the nucleus is firmly held and cannot be easily replaced. Under appropriate conditions, however, the halogen atom can be made to undergo some substitution reactions, as discussed below :

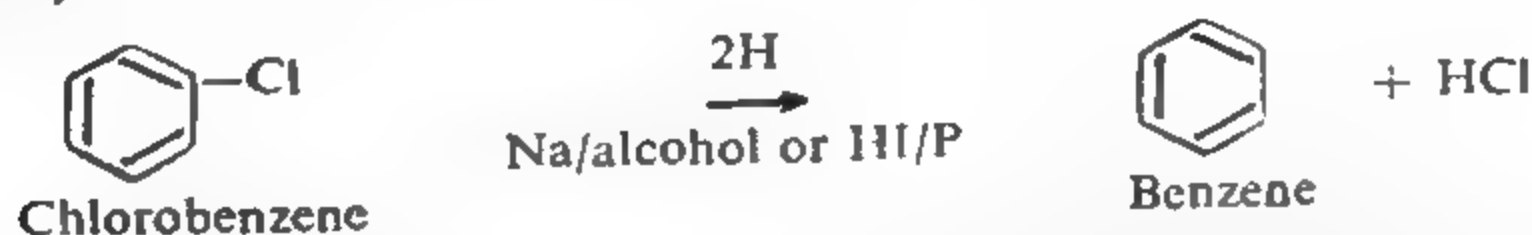
(i) **Replacement by an alkyl or aryl group. (Wurtz-Fittig's reaction).** In the presence of dry sodium in dry ether, the halogen atom can be easily replaced by an alkyl or an aryl group. For example,



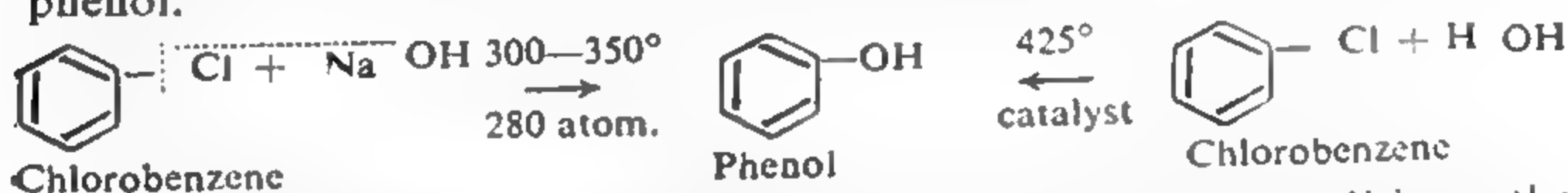
In (a), diphenyl and ethane are obtained as by-products and in (b) the yield is low. However, there is another method, called **Ullmann's Synthesis**, which is more suitable for preparation of diaryls. This method consists in heating an aryl iodide with copper powder in a sealed tube



(ii) **Replacement by a hydrogen atom (reduction).** The halogen atom can be replaced by hydrogen on treatment with sodium amalgam and alcohol or a mixture of hydrogen iodide and red phosphorus or with Ni/Al alloy in the presence of alkali to yield hydrocarbons. For example,



(iii) **Replacement by a hydroxyl group.** Under drastic treatment, the halogen atom can be replaced by a hydroxyl group. For instance, chlorobenzene when heated with a concentrated solution of sodium hydroxide at 300—350° under high pressure (about 280 atmospheres) or when heated with steam at 425° in the presence of a catalyst, gives phenol.



(iv) **Replacement by an amino group.** Under drastic conditions the halogen atom can also be replaced by an amino group. For instance, chlorobenzene when heated with aqueous ammonia at 280° under a pressure of 60 atmospheres, in the presence of Cu_2O , gives aniline.



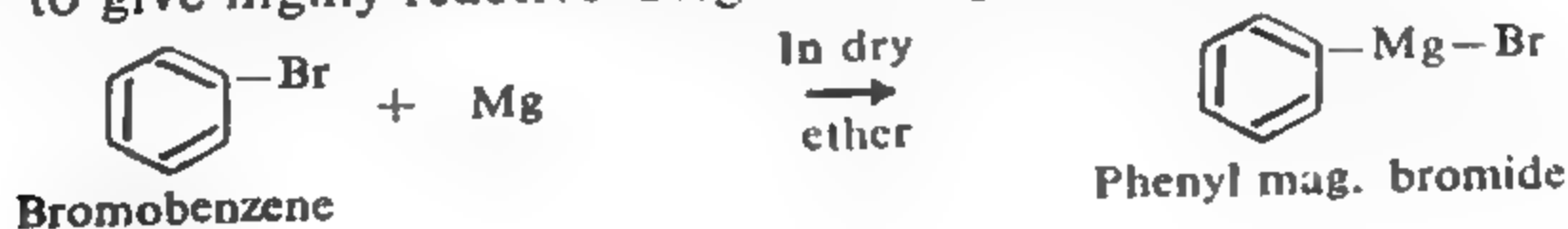
(v) **Replacement by cyanogen group.** The halogen atom can be replaced by a cyano group as well. For example, bromobenzene when heated with anhydrous cuprous cyanide in the presence of pyridine, gives cyanobenzene.



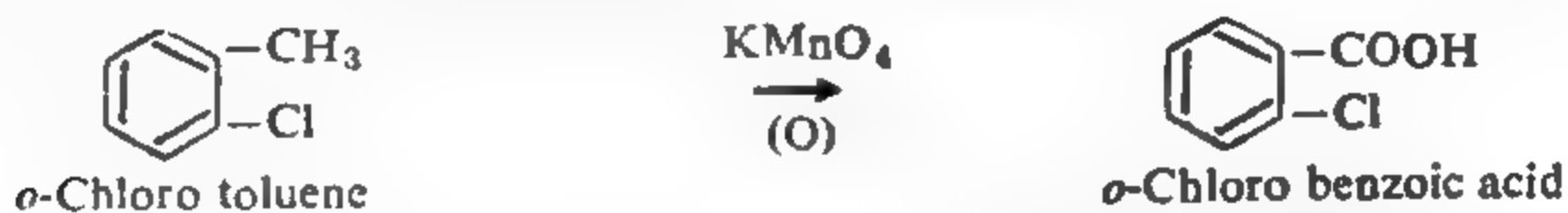
The presence of electronegative groups (e.g., $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, $-\text{Cl}$) in the ortho or para position with respect to the halogen atom renders the latter more mobile and it can be replaced much more easily by other groups.

(b) **Reactions of the Nucleus.** As usual, these halogen compounds can be nitrated, sulphonated, halogenated and alkylated.

(c) **Other Reactions.** (i) **Formation of Grignard reagents.** Bromo or iodo (but not chloro) benzene reacts with dry magnesium in dry ether to give highly reactive Grignard reagents. Thus,



(iii) **Oxidation.** The halogen compounds of the benzene homologues, on oxidation with potassium permanganate, yield compounds in which the halogen atoms remain intact and the side chain gets oxidised to the carboxyl group. For instance,



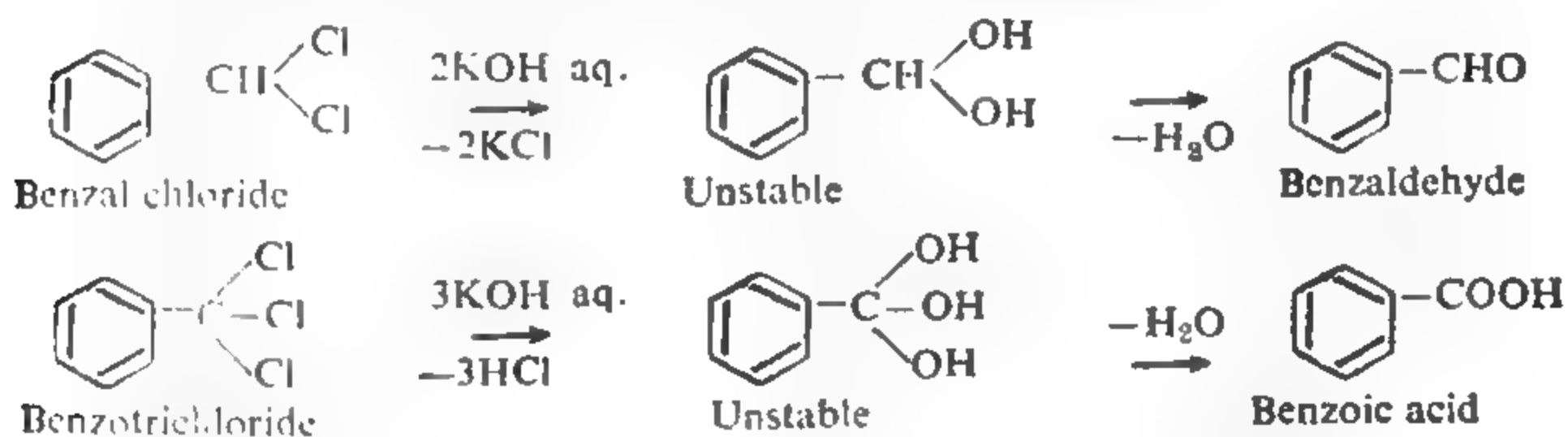
(B) Chemical Properties of Side Chain Halogen Derivatives.

As already mentioned, the side chain substituted halogen derivatives resemble alkyl halides in their chemical properties, that is, they undergo replacement reactions with the same ease as the alkyl halides, as illustrated below :

1. Replacement Reaction. (i) Replacement by hydroxyl group.



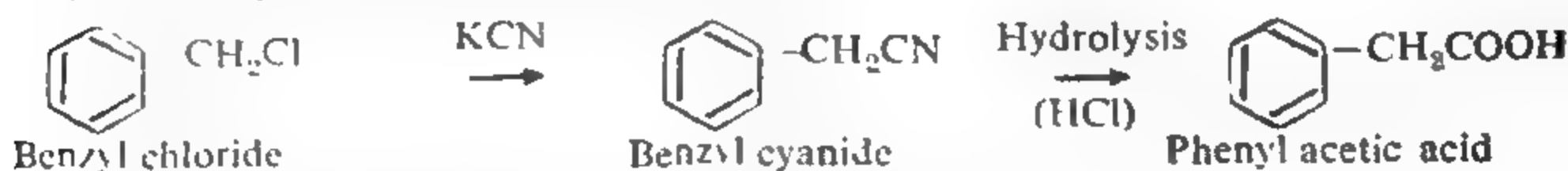
Benzal chloride and benzotrichloride on treatment with aqueous potash yield benzaldehyde and benzoic acid respectively.



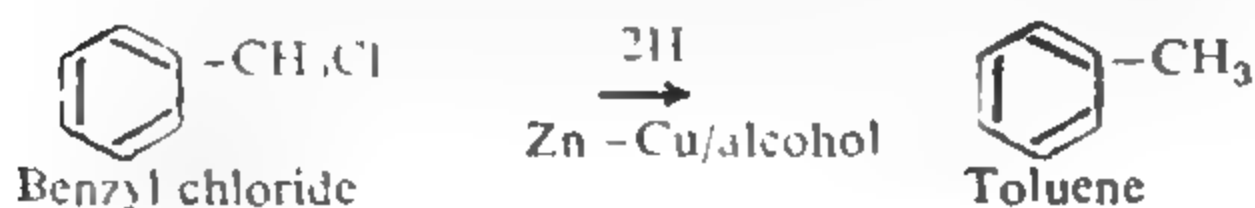
(ii) Replacement by amino group.



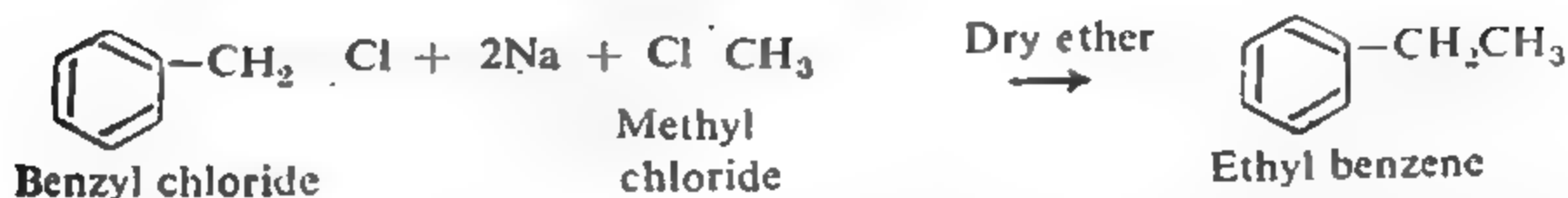
(iii) Replacement by cyano group.



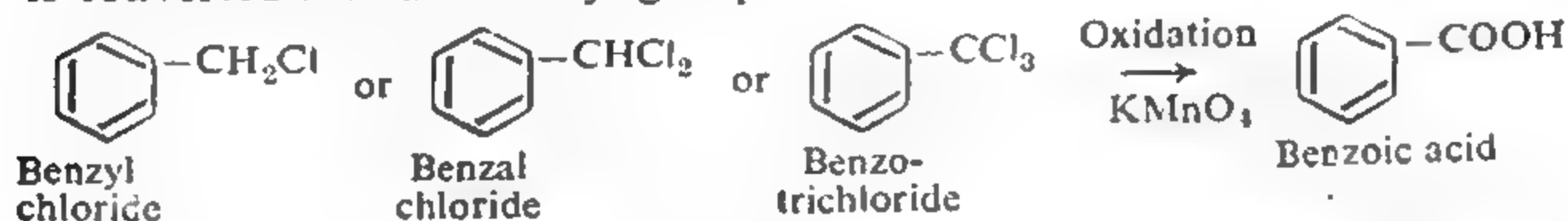
(iv) Replacement by hydrogen (reduction).



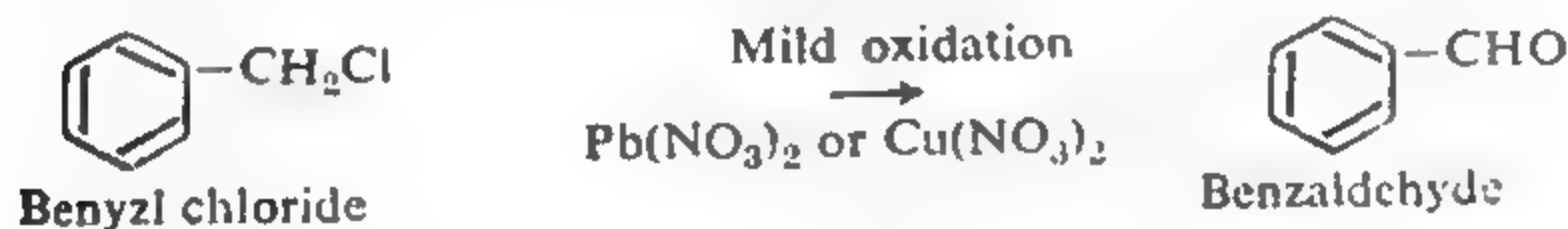
(v) Replacement by alkyl radical.



2. Oxidation. (i) On treatment with an oxidising agent (acidic KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ or HNO_3) the side chain including the halogen atom is converted into a carboxyl group.



(ii) With mild oxidising agents [$\text{Pb}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$], benzyl chloride is oxidised to benzaldehyde.



3. Reactions of the Nucleus. As usual, these halogen compounds can be nitrated, sulphonated, halogenated and alkylated, the new entrants occupying ortho and parapositions with respect to the halogenated side chain already present

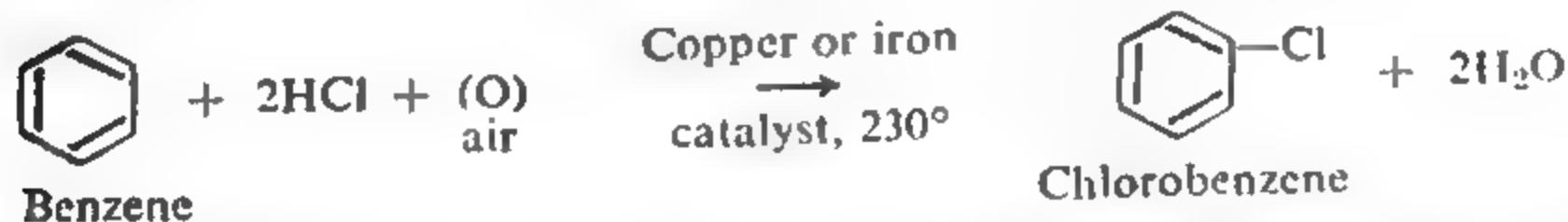
INDIVIDUAL MEMBERS

Chlorobenzene, Phenyl Chloride, $\text{C}_6\text{H}_5\text{Cl}$

Preparation. Chlorobenzene can be prepared by any of the general methods of preparing nuclear substituted halogen compounds.

In the laboratory, it is usually prepared either by the chlorination of benzene or from benzene diazonium chloride (see general methods).

Industrially, it is obtained by Raschig's process which consists in passing vapours of benzene, hydrogen chloride and air over a copper or iron catalyst at a temperature of 230° .



Properties. Chlorobenzene is a colourless liquid (b.p. 130° , sp. gravity 1.128) with an agreeable odour. It is insoluble in water but soluble in organic solvent.

Chemically it shows all the reactions of a nuclear substituted halogen compound. (See general properties).

Uses. (1) It is extensively used in the manufacture of D.D.T*, the well-known insecticide

(2) It is used for the manufacture of phenol, aniline and *p*-dichlorobenzene.

Bromobenzene or Phenyl Bromide, C_6H_5Br

Bromobenzene can be prepared by any of the general methods described earlier.

Laboratory Preparation. Bromobenzene is prepared in the laboratory by the bromination of benzene in the presence of a halogen carrier, but in the absence of sunlight. The details of the process are as follows :

An apparatus, as shown in Fig. 1, is fitted up. About 78 gm. of benzene is taken in the round-bottomed flask, along with about 2-3 gm. of pure iron powder. Bromine (160 gm) is added dropwise from the dropping funnel, through the condenser. The reaction takes place and the hydrogen bromide formed is led into a beaker containing water through an inverted funnel. After the contents cool down to room temperature, the reaction mixture is washed successively with sodium hydroxide solution and water, separated by a separating funnel, dried and then purified by distillation. The fraction distilling over between $150-125^\circ$ is pure bromobenzene

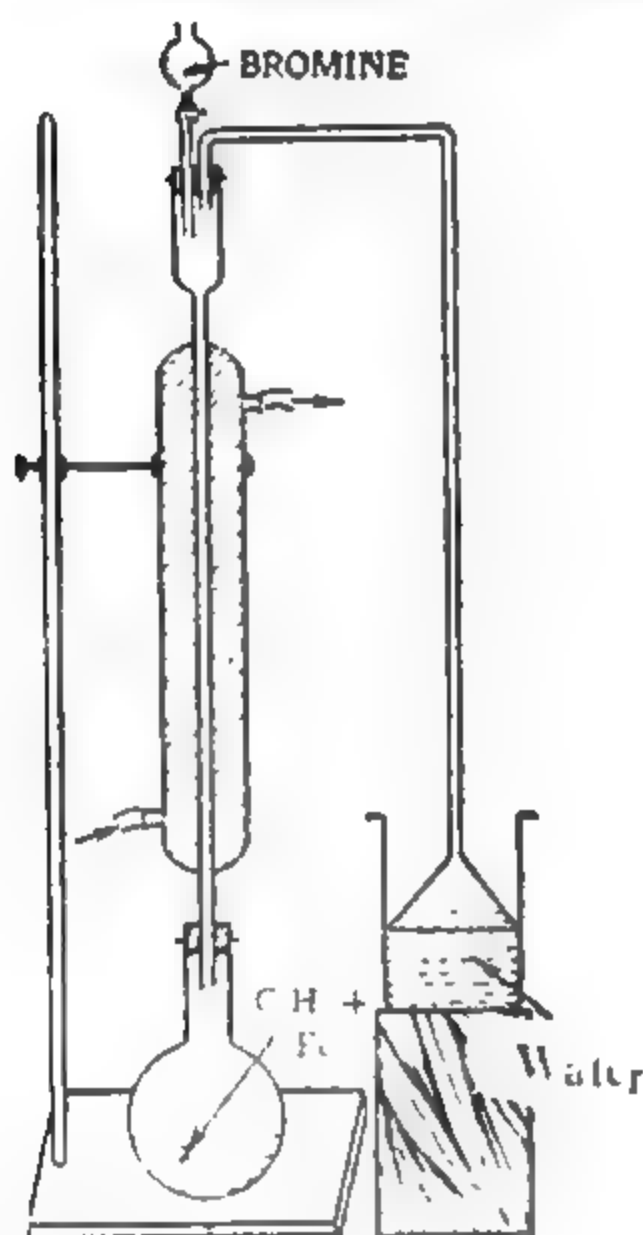


Fig 1 Preparation of Bromobenzene

Properties. Bromobenzene resembles chlorobenzene in physical and chemical properties.

Iodobenzene, Phenyl Iodide, C_6H_5I

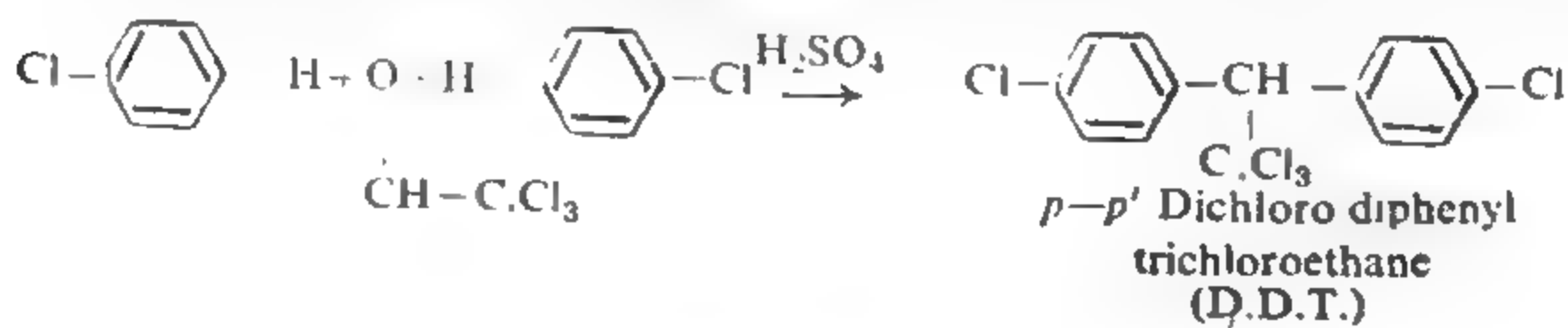
Iodobenzene can be prepared in the laboratory by heating benzene and iodine in a sealed tube in the presence of an oxidising agent like concentrated nitric acid. It can be prepared more conveniently by heating benzene diazonium chloride with potassium iodide.

Properties. Iodobenzene is a colourless heavy liquid boiling at 188° . It is more reactive than chlorobenzene or bromobenzene.

Benzyl Chloride, Phenyl methyl chloride, $C_6H_5CH_2Cl$

It is a typical side chain substituted halogen derivative. It may be

*Chlorobenzene combines with chloral in the presence of concentrated sulphuric acid to give *p,p'*-Dichloro-Diphenyl-Trichloroethane, (D.D.T.).



prepared in the laboratory by passing chlorine into boiling toluene in the presence of sunlight till the required increase in weight occurs. Benzyl chloride is then separated by fractional distillation.

Properties Benzyl chloride is a colourless liquid boiling at 178° with an unpleasant odour. It is strongly lachrymatory (*i.e.*, having an irritating effect on the membranes of eyes and nose). It is insoluble in water but soluble in organic solvents.

Chemically, it resembles the alkyl halides. The halogen atom can be easily replaced by various groups like, hydroxyl, amino, cyanogen, etc.

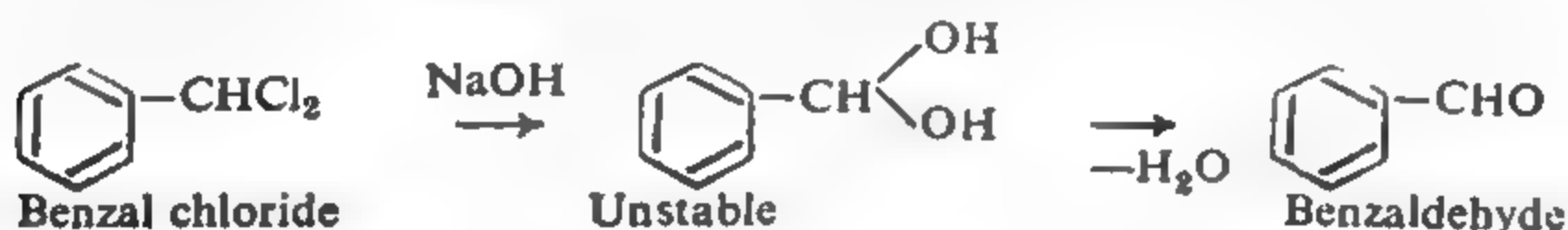
Uses. Its chief use lies in the manufacture of benzoic acid, benzaldehyde, benzyl alcohol, benzylamine, etc.

Benzal Chloride, Benzyldiene Chloride, $C_6H_5CHCl_2$

This compound is prepared by passing the requisite amount of chlorine through toluene or by the action of phosphorus pentachloride on benzaldehyde.



Properties. Benzal chloride is a colourless liquid, boiling at 206° . It can be readily hydrolysed by aqueous alkali to benzaldehyde.

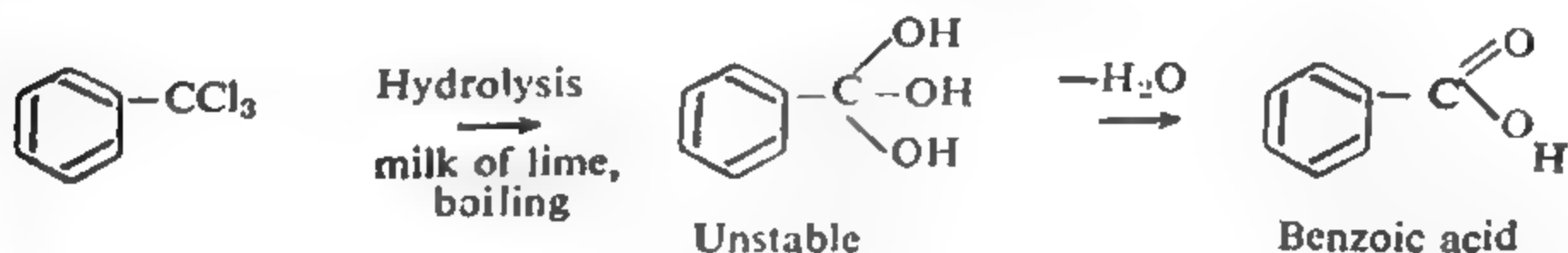


Uses. It is mainly used for the preparation of benzaldehyde which is a very important article of commerce in the preparation of dyes and drugs.

Benzotrichloride $C_6H_5CCl_3$

It is obtained by prolonged chlorination of boiling toluene till all the three hydrogen atoms of methyl group are replaced by chlorine atoms.

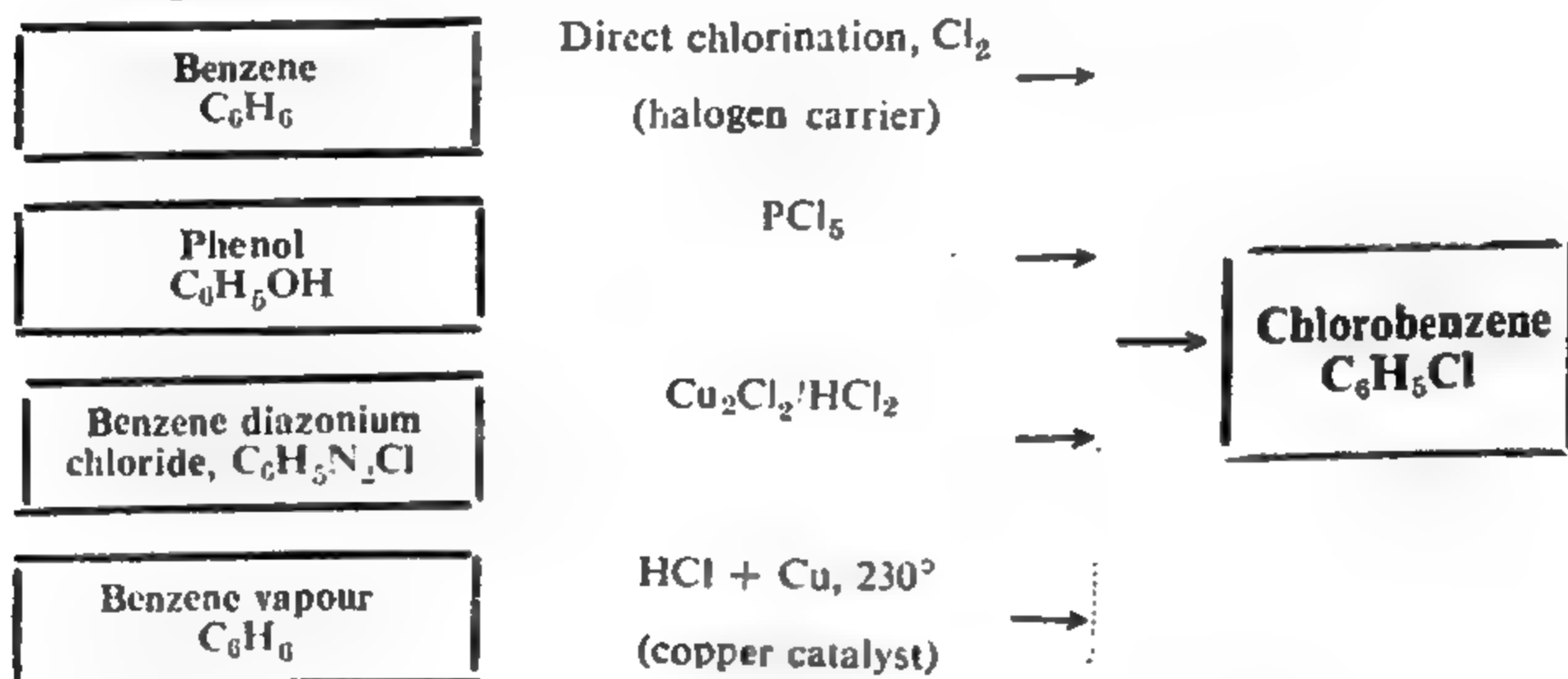
It is a colourless liquid boiling at 213° . With alkali [milk of lime, $Ca(OH)_2$] it is hydrolysed to give benzoic acid.



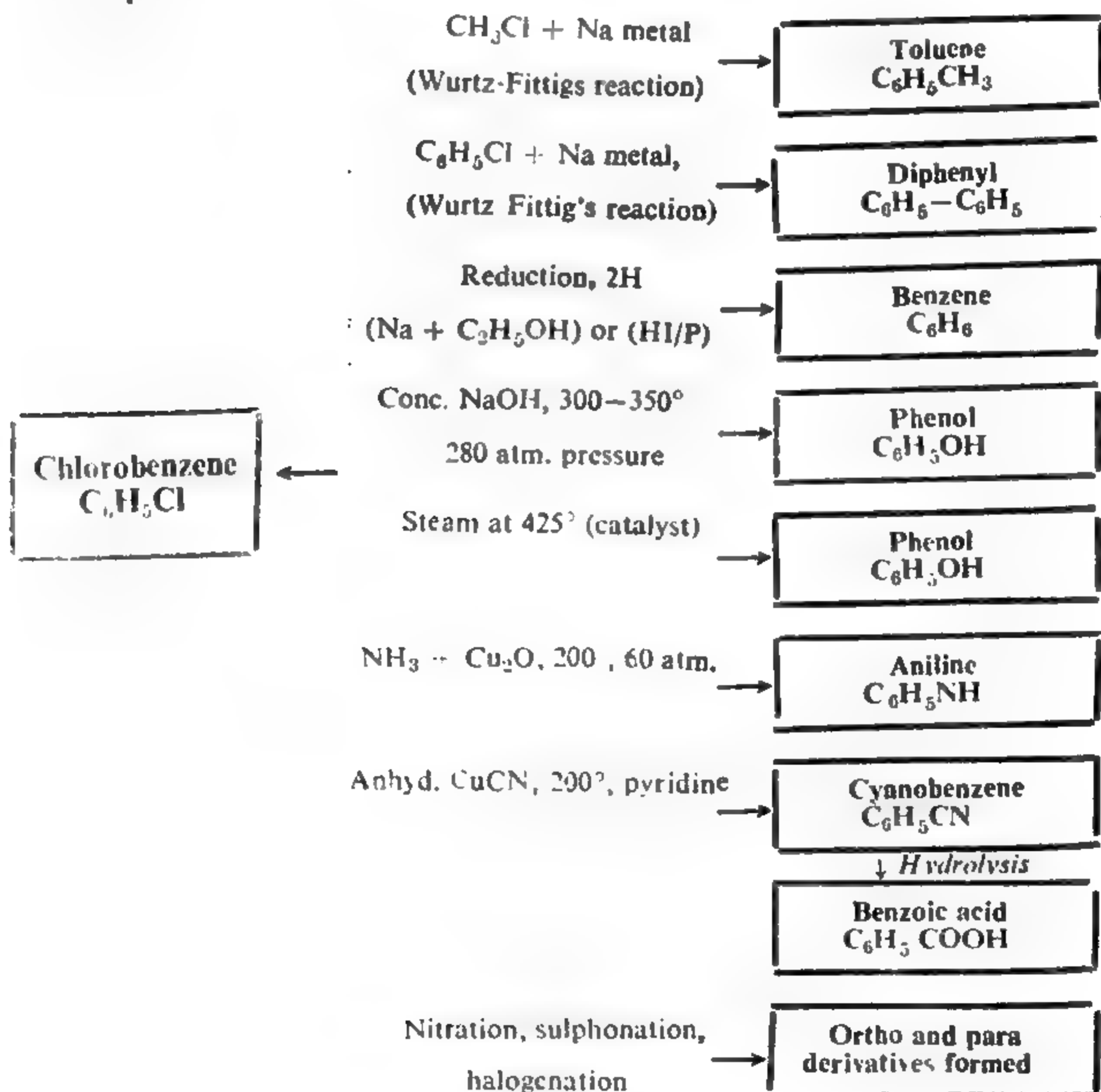
It is employed, on a commercial scale, for the manufacture of benzoic acid.

SUMMARY OF TYPICAL MEMBERS
PREPARATION AND PROPERTIES OF CHLOROBENZENE

Preparation.

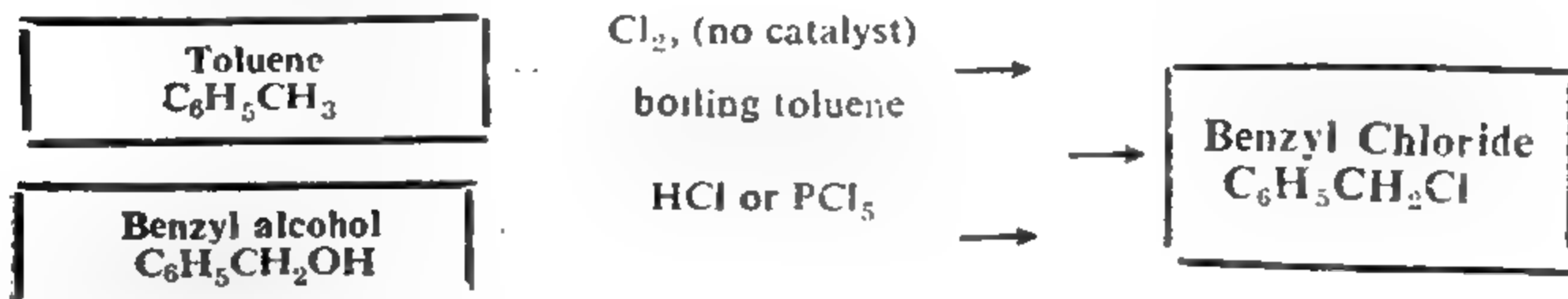


Properties.

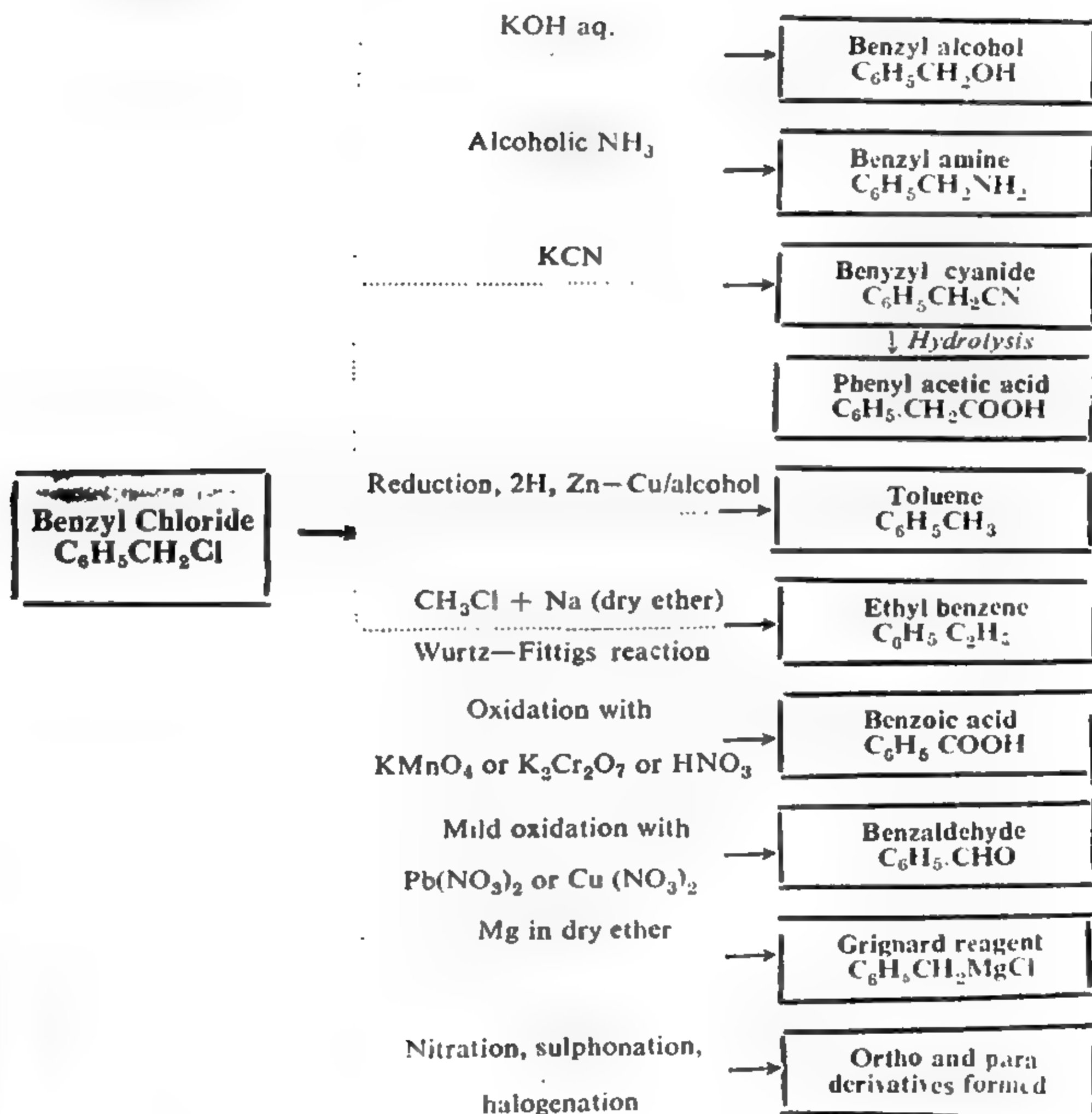


PREPARATION AND PROPERTIES OF BENZYL CHLORIDE

Preparation.



Properties.



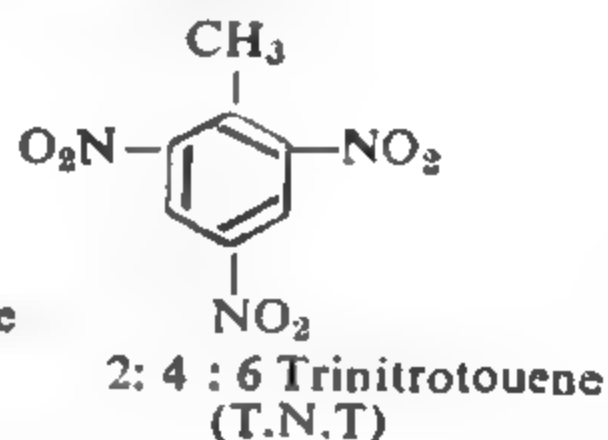
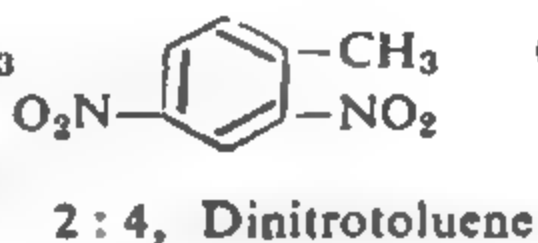
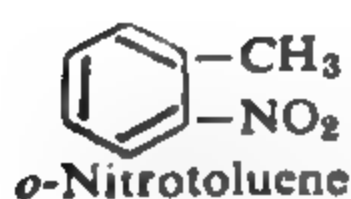
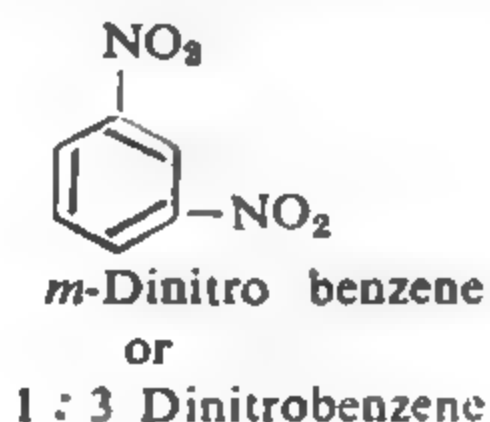
QUESTIONS

1. Describe the methods to introduce a halogen atom in (a) side chain. (b) nucleus. How do these two types of compounds differ from each other?
2. Give the general methods of preparation and properties of aromatic halogen compounds.
3. Write notes on :
 (a) Bromobenzene (b) Iodobenzene (c) Benzyl chloride (d) Benzal chloride Benzotrichloride.
4. How do the properties of aryl halides differ from those of alkyl halides?
5. Give in each case four important properties of Nuclear and Side chain halogen derivatives of aromatic hydrocarbons.
(Panjab Inter 1961)
6. By what methods can halogen group be introduced (a) in the nucleus (b) in the side chain of an aromatic hydrocarbon? Describe the difference in properties of the compounds formed. What difficulty is experienced in preparing the iodo derivatives and how can this be overcome?
7. Explain giving equations wherever possible what happens when :
 (a) Chlorine is passed into boiling benzene,
 (b) Alcoholic potassium cyanide is added to (i) Chlorobenzene (ii) Ethyl Iodide.
(Panjab Inter 1953 S)
8. What do you understand by the term 'Ring' and 'Chain' substitutions? Illustrate your answer by comparing the properties of chlorobenzene and benzyl chloride. How do you account for the difference, if any?
(Panjab Inter 1952)
9. (a) Give points of difference for Nuclear and Side chain aromatic halogen compounds.
(Panjab Inter 1960 S)

CHAPTER XLVII

AROMATIC NITRO COMPOUNDS

As mentioned earlier, compounds containing one or more nitro ($-\text{NO}_2$) groups attached directly to the benzene nucleus (in place of hydrogen atoms) are called **aromatic nitro compounds**. A few important nitro-derivatives of benzene and toluene are :



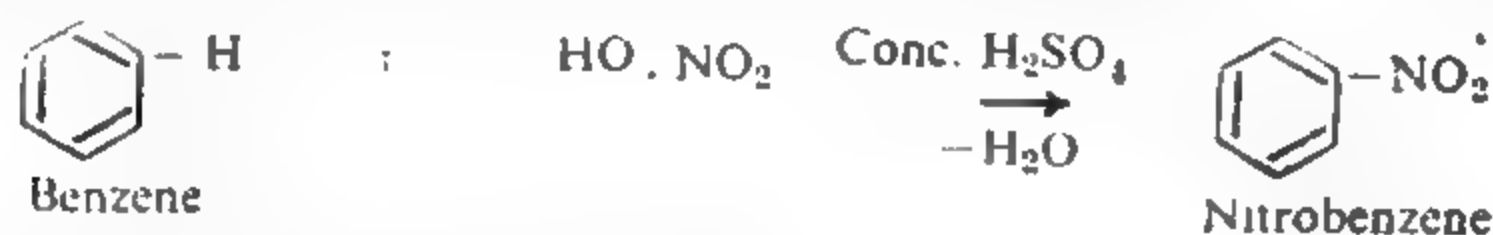
The process of replacing one or more hydrogen atoms of the benzene nucleus by the nitro ($-\text{NO}_2$) groups (i.e., introducing nitro groups into the aromatic nucleus) is called **nitration** and the reagent used for the purpose is called **nitrating reagent**.

The number of nitro groups introduced depends upon :

- (i) The nitrating reagent
- (ii) Temperature of nitration
- (iii) The nature of the compound to be nitrated.

(i) **The nitrating reagent used.** Common nitrating reagent used for introducing one nitro group is a mixture of concentrated nitric acid and concentrated sulphuric acid. Stronger nitrating agents employed are : fuming nitric acid and concentrated sulphuric acid ; a mixture of concentrated nitric acid and acetic anhydride ; nitrogen dioxide and anhydrous aluminium chloride (catalyst) ; acetyl nitrate, $\text{CH}_3\text{CO.O.NO}_2$. The last reagent is more suitable for introducing only one $-\text{NO}_2$ group in ortho position. However, its explosive nature (on heating) renders it unsuitable to be used.

The function* of concentrated sulphuric acid and acetic anhydride is to absorb the water formed during the reaction.



(ii) **Temperature of nitration.** If nitration is carried out below 60° , only one nitro group is introduced. Two nitro groups are usually introduced when the reaction is carried out between 60° and 100° . Three groups may be introduced at temperatures above 100° .

(iii) **The nature of the compounds to be nitrated.** Generally speaking, the presence of ortho and para directing groups (e.g., $-\text{CH}_3$, $-\text{OH}$ or $-\text{NH}_2$) in the nucleus, facilitates nitration, whereas the presence of meta-directing groups (e.g., $-\text{NO}_2$, $-\text{COOH}$, $-\text{CN}$) retards further nitration.

Physical Properties. (i) Generally, the nitro compounds are pale-yellow liquids or crystalline solids, with a characteristic odour.

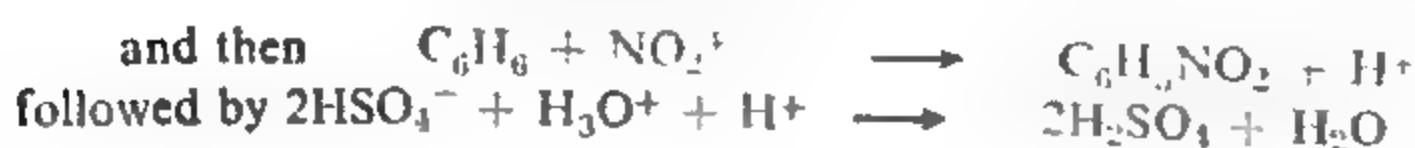
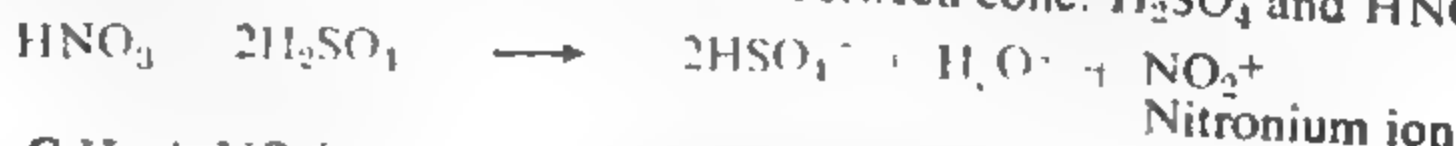
(ii) The aromatic nitro compounds are heavier than and immiscible with water, but they are freely soluble in organic solvents.

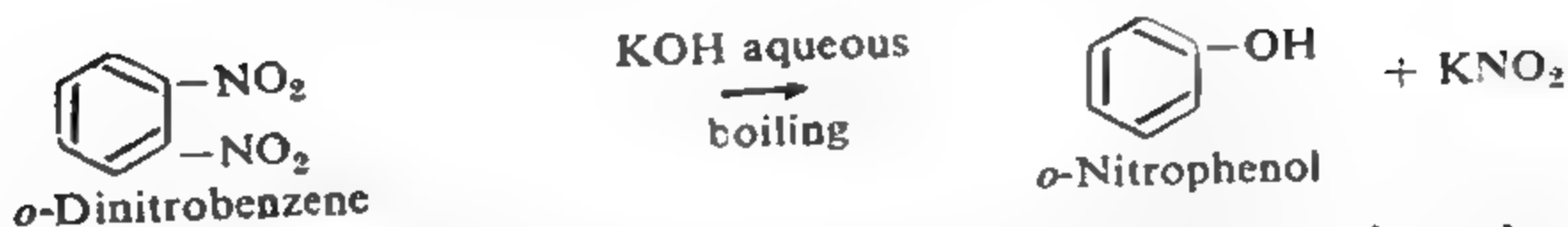
(iii) They are volatile in steam.

(iv) They explode on strong heating or when detonated. They are, therefore, used in bombs, dynamite, etc.

Chemical Properties As a rule, the nitro group is firmly attached to the benzene nucleus and does not undergo replacement reactions. However, if more than one nitro groups are present in the nucleus or a halogen atom is also present along with, then one of them can be easily replaced. Thus :

*Modern research has established that the function of conc. H_2SO_4 is more than a mere dehydrating agent. It is assumed that the real nitrating agent is the nitronium ion, NO_2^+ , which is formed by interaction between conc. H_2SO_4 and HNO_3 .





The only important reaction a nitro group undergoes is its **reduction**. The nitro group can be easily reduced to an amino group ($-\text{NH}_2$) with zinc and hydrochloric acid or tin and hydrochloric acid. But with other reducing agents like zinc dust and ammonium chloride or sodium and methyl alcohol or zinc dust and sodium hydroxide, the reduction is only partial and compounds like nitrosobenzene ($\text{C}_6\text{H}_5\text{NO}$), phenyl hydroxylamine ($\text{C}_6\text{H}_5\text{NHOH}$) or azobenzene ($\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$) are formed. The nature of the reducing agent (acidic, alkaline or neutral) employed determines the end product. (For details see reduction of nitrobenzene).

INDIVIDUAL MEMBERS

NITROBENZENE, OIL OF MIRBANE, $\text{C}_6\text{H}_5\text{NO}_2$

Nitrobenzene was first isolated by Mischerlich in 1834.

Preparation. It can be prepared in laboratory or industry by nitration of benzene at temperatures below 60° , with a mixture of concentrated nitric acid and concentrated sulphuric acid (*nitrating reagent*).



Details of the method. About 60 c.c. of benzene are added in very small instalments (2–3 c.c. each time) to a well-cooled mixture of concentrated sulphuric acid (60 c.c.) and conc. nitric acid (60 c.c.) taken in a round-bottomed flask of one litre capacity. Care is taken that the temperature of the reagents, after each addition, does not shoot up beyond $55-60^\circ$, otherwise there is likelihood of dinitrobenzene being formed. To avoid the rise of temperature the round bottomed flask is immersed in cold water and shaken thoroughly. When the whole of benzene has been added (this process takes 30–40 minutes) the contents are heated under a reflux condenser with frequent stirring in a water bath below $55-60^\circ$ for about 45 minutes. During this time, usually the nitration is complete. The contents are then cooled and poured into a large amount of water, when nitrobenzene separates as a heavy oil, the nitrobenzene layer is separated by a separating funnel, washed with water and sodium carbonate solution and finally again with water. It is kept over anhydrous calcium chloride and distilled using an air condenser. The fraction coming over at about $80-81^\circ$ is unreacted benzene and is collected separately. Afterwards, the temperature suddenly goes up and the fraction distilling over between $205-210^\circ$ is pure nitrobenzene.

Caution. Nitrobenzene is not distilled to dryness as the black residue is a polynitro-compound and explodes violently on heating.

Commercially, nitrobenzene is a very important intermediate for the preparation of dyes, drugs, etc., and it is prepared by the same method

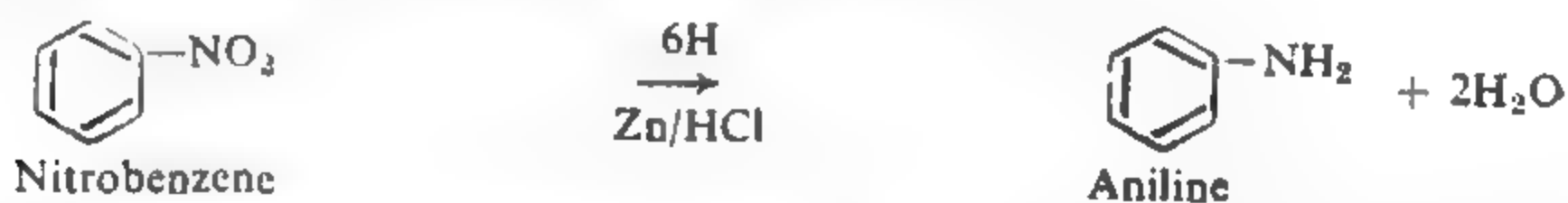
as above, except for the difference that nitration is carried out in a big pan fitted with a mechanical stirrer and a set of pipes through which cold water or steam can be passed (cf. Fig. 1). After nitration, the contents are drawn and treated as usual.

Physical Properties. Nitrobenzene is a pale-yellow liquid, with a strong smell of bitter almonds. It boils at 210° . It is volatile in steam; insoluble in water, but soluble in organic solvents like alcohol and ether.

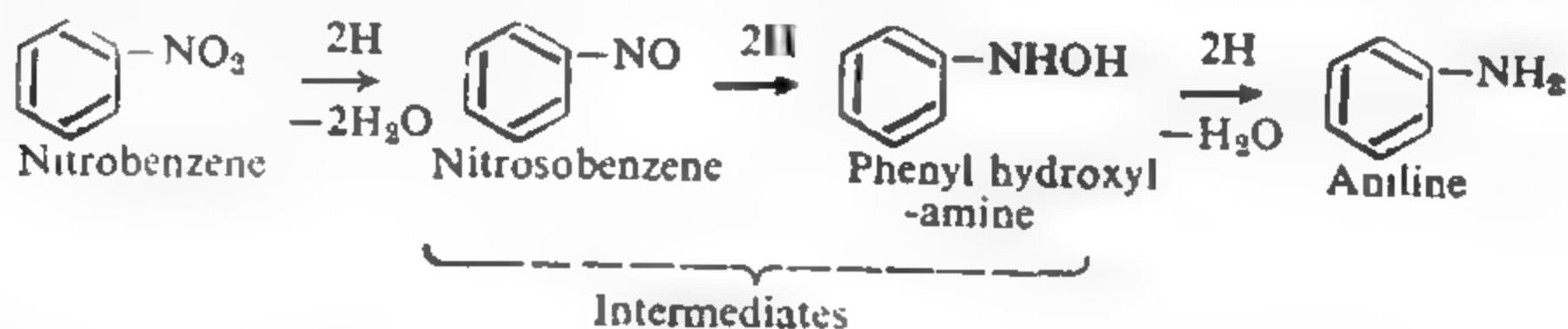
Chemical Properties. Nitrobenzene has very few properties, as the nitro group is firmly attached to the nucleus and is not easily replaceable.

The most important property of the nitro group is its *reduction*, which can be carried out in an *acidic*, *neutral* or an *alkaline medium*. In each case different products are obtained

(a) **Reduction in acid medium.** When nitrobenzene is reduced by zinc and hydrochloric acid, aniline is obtained.



It is assumed that the above reaction takes place through the following steps :



The intermediate compounds, nitrosobenzene and phenyl hydroxylamine, cannot be isolated from an acid solution.

Other acid reducing media are tin and hydrochloric acid, stannous chloride and hydrochloric acid or zinc and acetic acid. On an industrial scale, iron and hydrochloric acid is used.

(b) **Reduction in neutral medium.** In a neutral reducing medium like zinc dust and ammonium chloride or water, nitrobenzene is reduced to phenyl hydroxylamine.

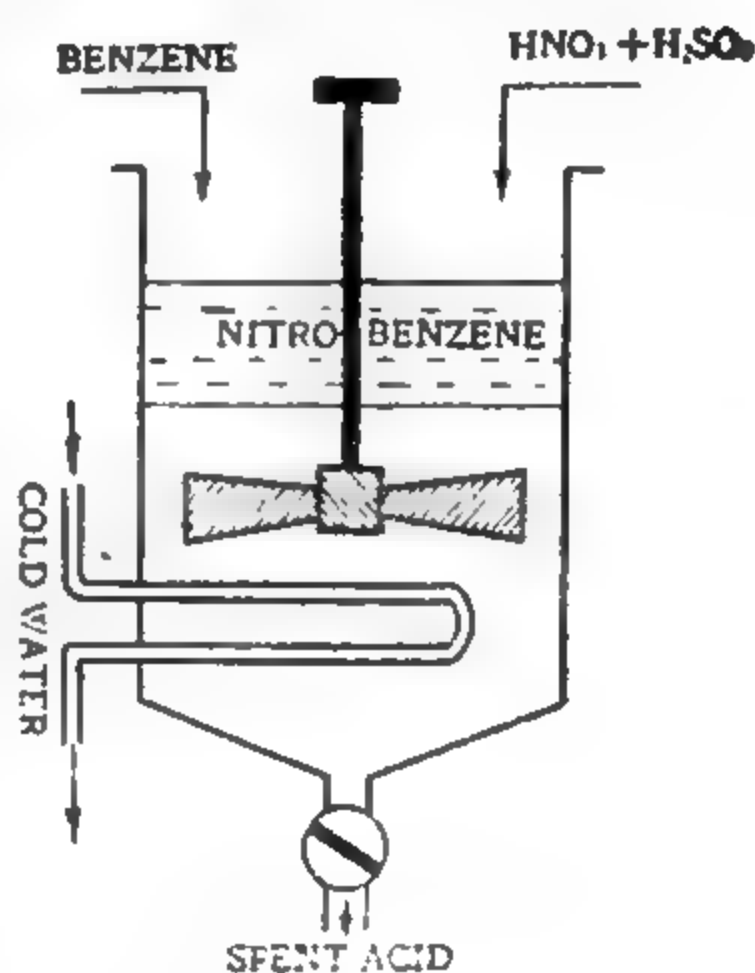
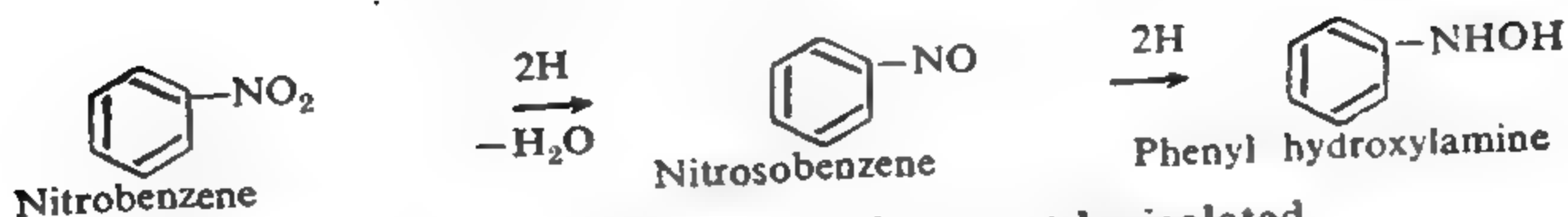
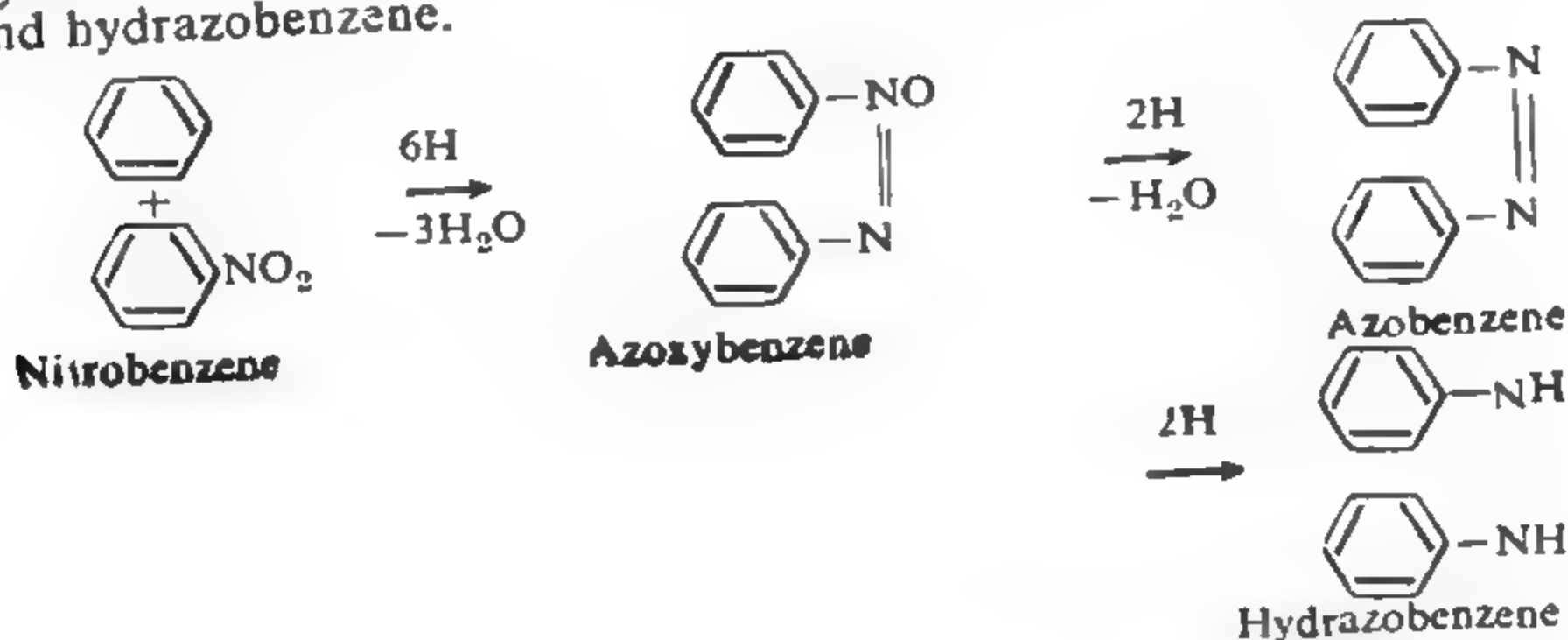


Fig. 1. Manufacture of Nitrobenzene



Nitrosobenzene is so shortlived that it cannot be isolated.

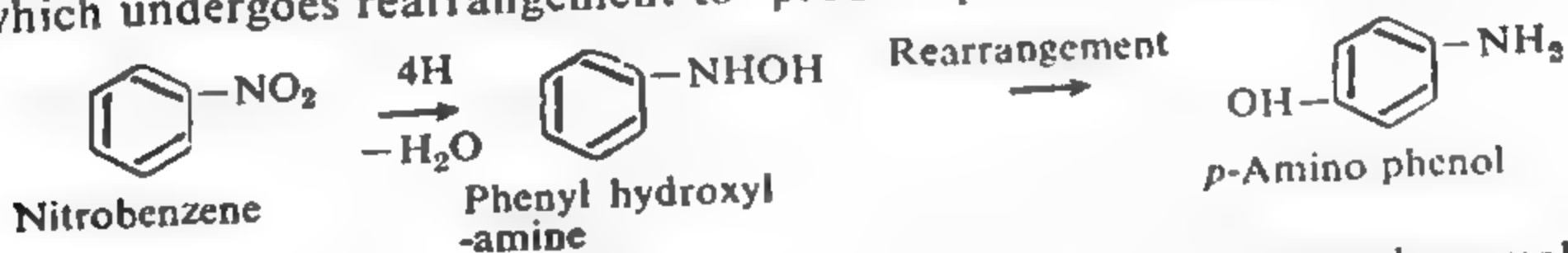
(c) **Reduction in alkaline medium.** With alkaline reducing agents like stannous chloride and sodium hydroxide, or zinc dust and sodium hydroxide, nitrobenzene yields successively azoxybenzene, azobenzene and hydrazobenzene.



All the three reduction products, *viz.*, azoxybenzene, azobenzene and hydrazobenzene have been isolated, employing suitable reducing agents.

When any one of the above intermediate products (such as nitrosobenzene, phenyl hydroxylamine, azoxybenzene, etc.) is reduced in *acidic medium*, aniline is obtained.

(d) **Electrolytic reduction.** Nitrobenzene, when reduced electrolytically in strong sulphuric acid medium, yields phenyl hydroxylamine, which undergoes rearrangement to produce *p*-amino phenol.



Reactions of Benzene Nucleus. Nitrobenzene undergoes the usual reactions of aromatic nucleus, that is, chlorination, sulphonation and nitration. In each case the corresponding meta product results (*cf.* Crum Brown and Gibson's Rule). The products obtained are :



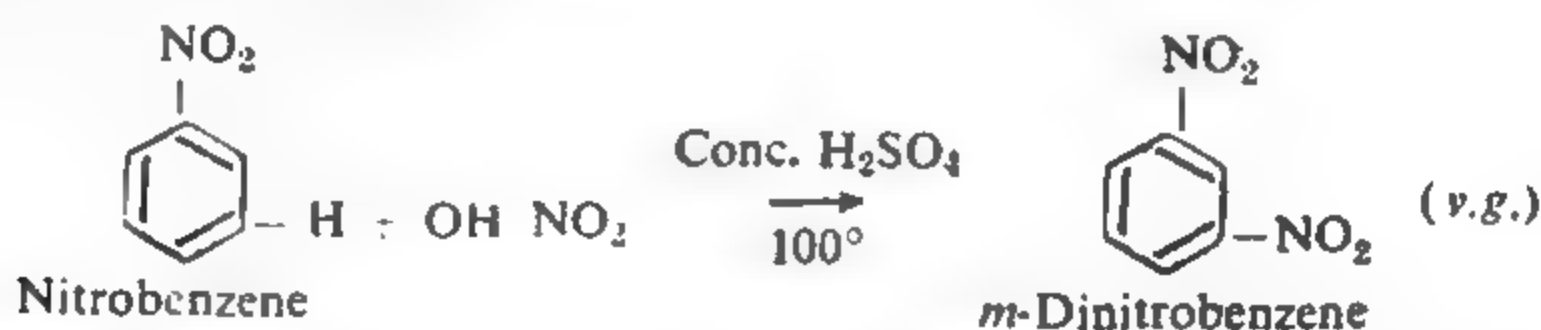
Uses. The most important use of nitrobenzene is in the preparation of aniline.

It is also used in the manufacture of boot polishes (since it penetrates the leather very easily), and for scenting cheap soaps.

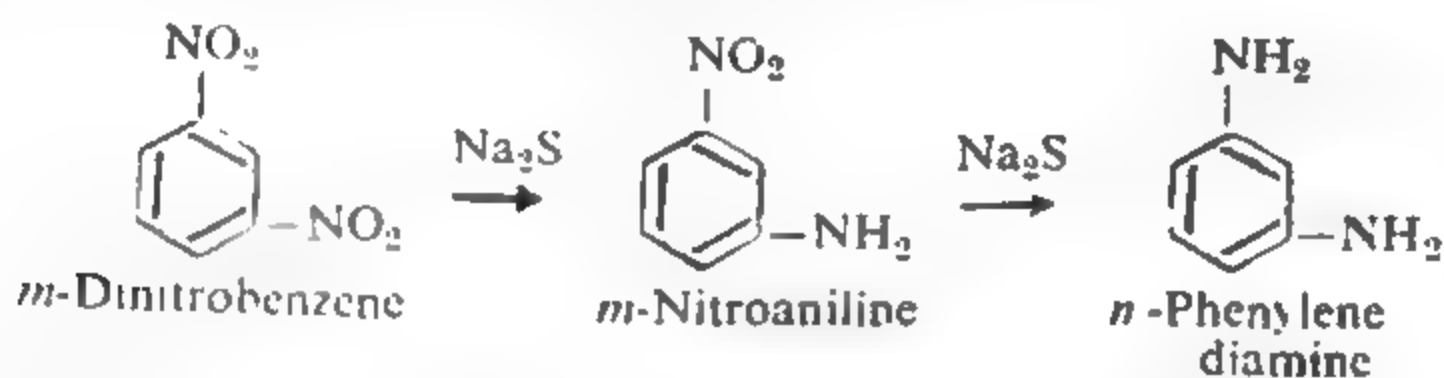
In laboratory, it is used as an oxidising agent.

m-Dinitrobenzene, $C_6H_4(NO_2)_2$

m-Dinitrobenzene is prepared by further nitration of nitrobenzene with a mixture of concentrated sulphuric acid and fuming nitric acid. After the reagents have been slowly mixed up, they are heated on a boiling water bath for an hour, with frequent shaking. Afterwards the contents are poured in excess of cold water, when *m*-dinitrobenzene separates out as a yellow crystalline solid, which may be purified by recrystallisation from alcohol.



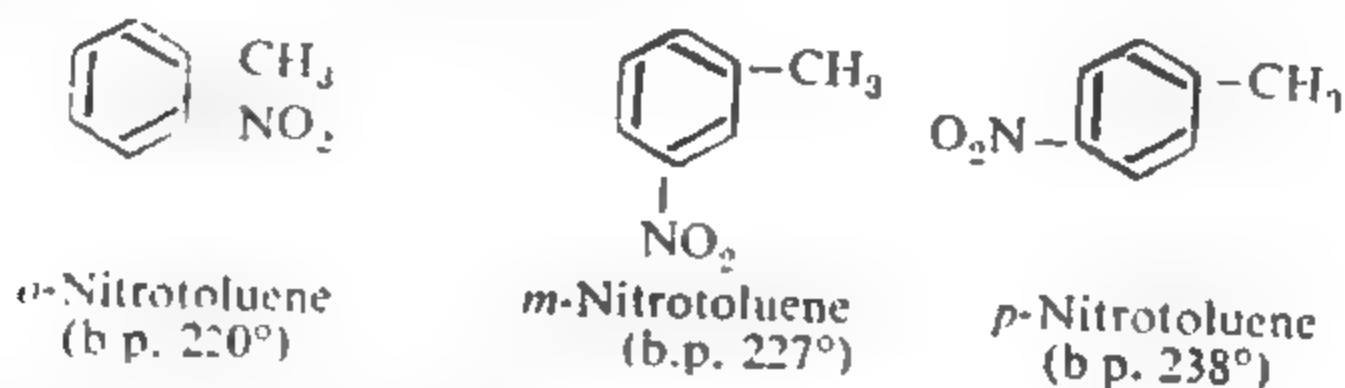
Properties. *m*-Dinitrobenzene is a pale-yellow solid (m.p. 90°) insoluble in water but soluble in organic solvents and volatile in steam. Chemically, *m*-dinitrobenzene is similar to nitrobenzene. It can be reduced with alcoholic ammonium sulphide or sodium sulphide first to *m*-nitroaniline and then to *m*-phenylenediamine.



Uses. It is used in the manufacture of important dye stuffs like *Bismark Brown* (used in boot polishes) and explosives.

Nitro-Toluenes, $CH_3.C_6H_4.NO_2$

Three nitrotoluenes (*i.e.* *o*-, *m*- and *p*-) are possible and all the three are known.



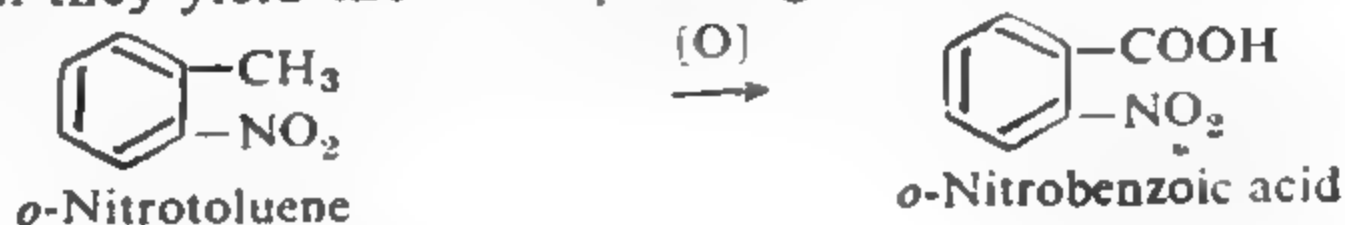
Toluene can be nitrated more readily than benzene due to the activating influence of methyl group.

Nitration of toluene is carried out simply by pouring it in a mixture of nitric acid and fuming sulphuric acid when *o*- and *p*-isomers are the

main products (*cf.* Crum Brown and Gibson's rule). These are separated by fractional distillation. *m*-Nitrotoluene is prepared indirectly. All the nitrotoluenes can be reduced to the corresponding toluidines. For example,



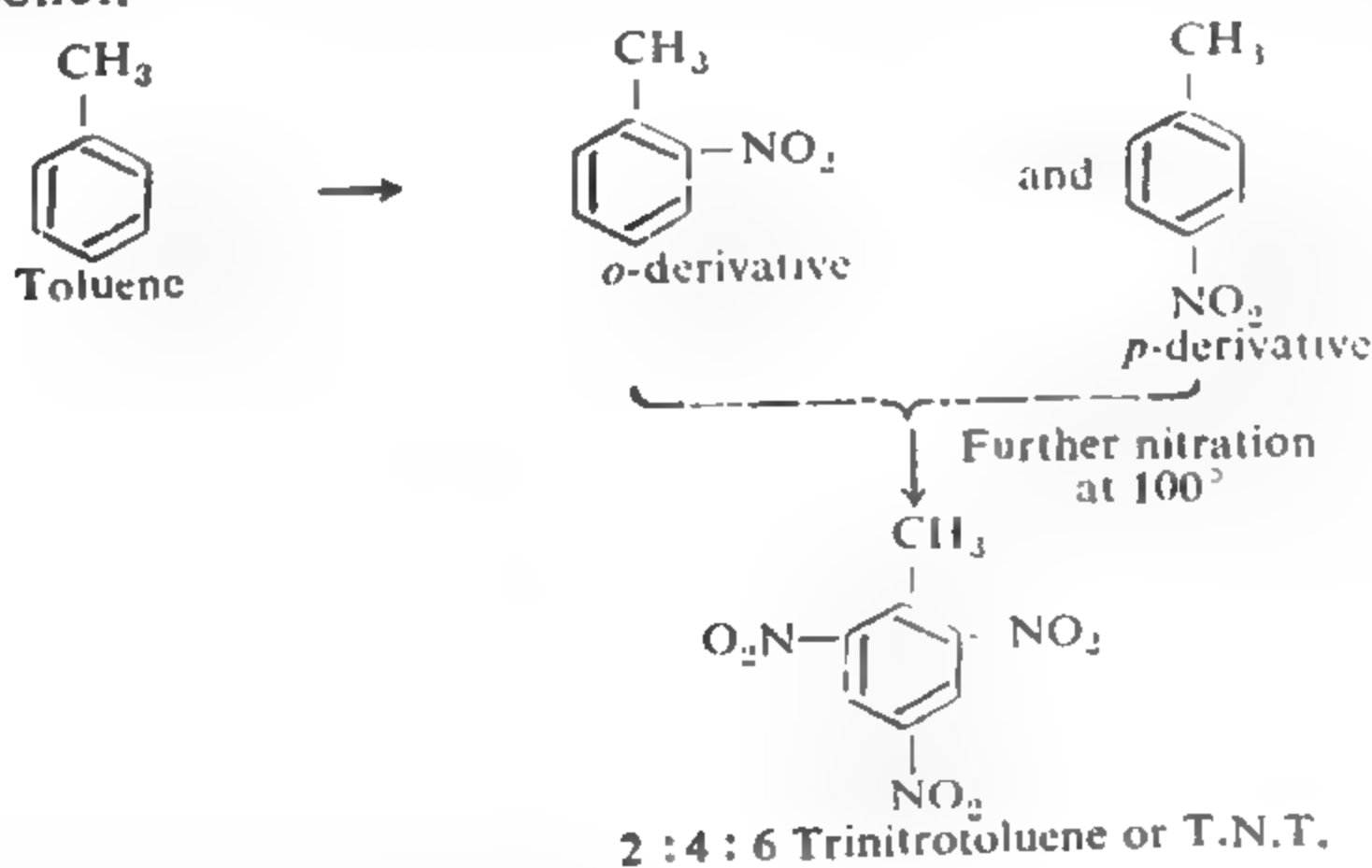
They can be readily nitrated further to yield di- and trinitrotoluenes. On oxidation they yield the corresponding carboxylic acids.



They are used for the manufacture of the well-known explosive, T.N.T.

Trinitrotoluene, or T.N.T., $\text{CH}_3\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$

2 : 4 : 6 Trinitrotoluene or T.N.T., as it is commonly called, is the ultimate product obtained by the nitration of toluene. Toluene is nitrated by dropping in a mixture of concentrated nitric acid and fuming sulphuric acid, with frequent stirring. The ortho and para nitrotoluenes first obtained are further nitrated at 100° , when T.N.T. is obtained. The ultimate product is washed with water and re-crystallised from alcohol.



T.N.T. is a pale-yellow crystalline compound (m.p. 81°). It explodes violently on burning or when detonated. $2\text{CH}_3\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3 \rightarrow 12\text{CO} + 3\text{N}_2 + 4\text{H}_2$. It is, therefore, used for military purposes in bombs, shells and torpedoes. For example, *amatol* (a mixture of

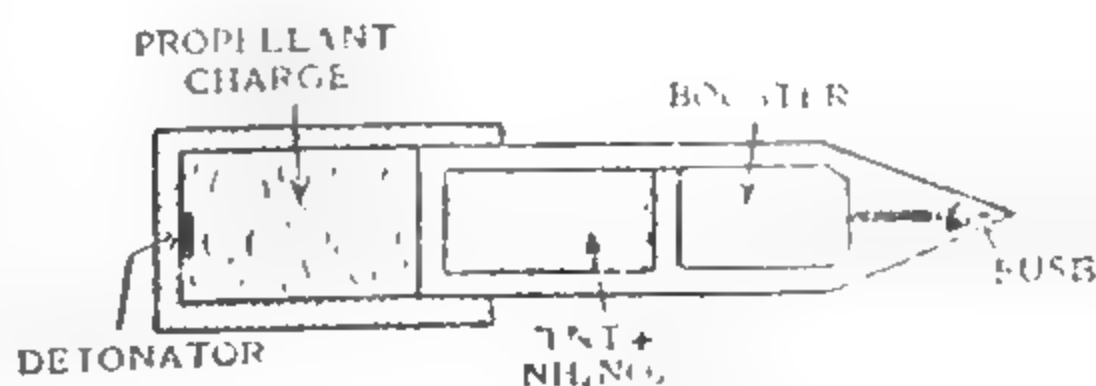


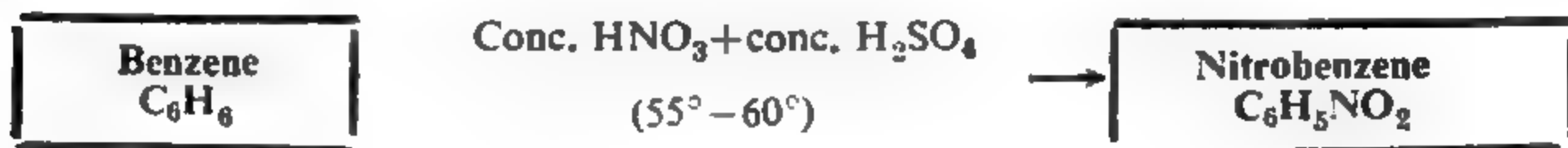
Fig 2. T.N.T. bomb

T.N.T. and ammonium nitrate) is used for blasting purposes (see (Fig. 2).

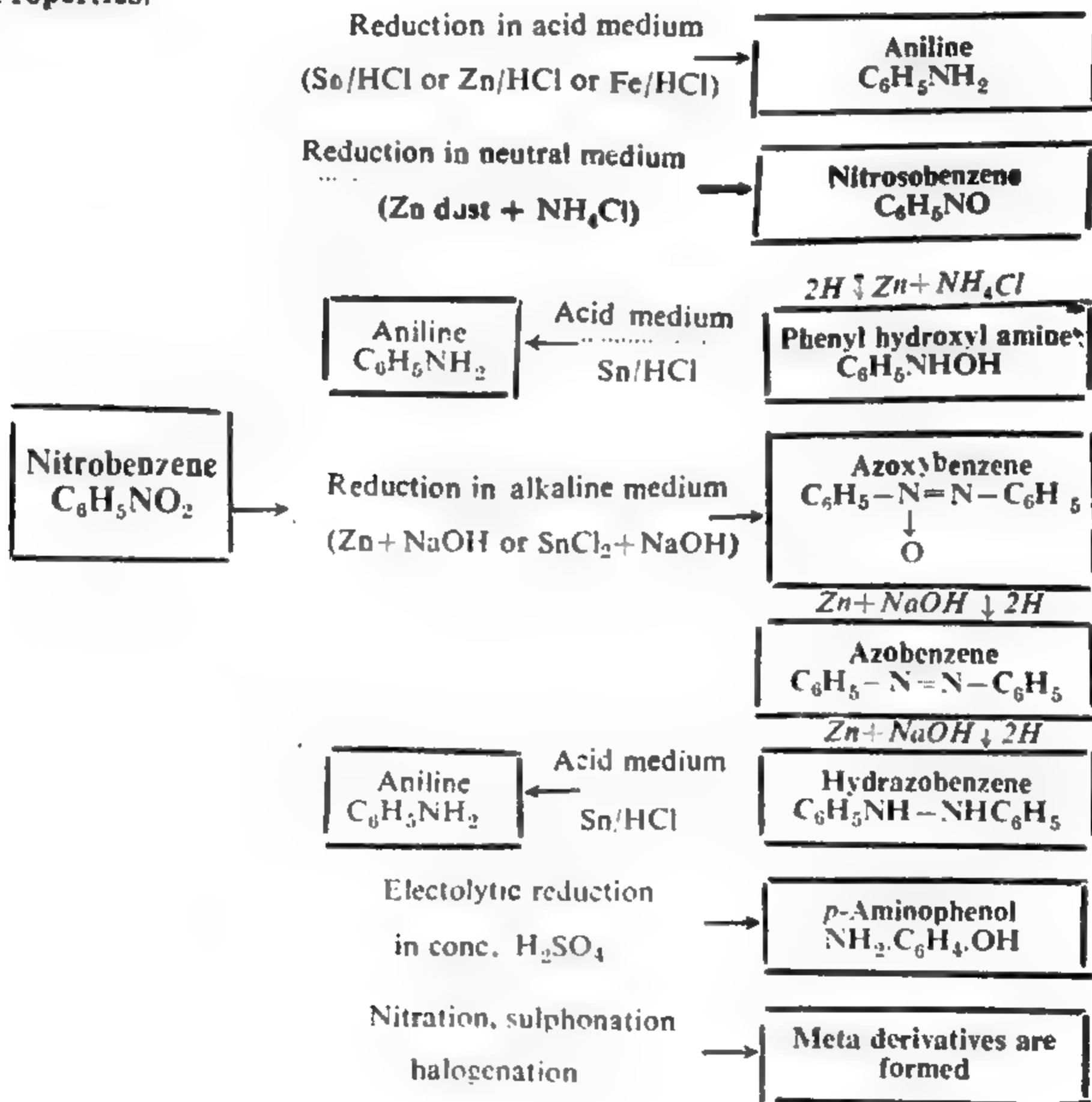
SUMMARY OF A TYPICAL MEMBER

PREPARATION AND PROPERTIES OF NITROBENZENE

Preparation.



Properties.



QUESTIONS

1. What do you understand by the term 'Nitration'? Describe the general methods used for nitration of aromatic compounds.
2. How can you effect the nitration of (a) benzene (b) phenol (c) toluene? What are the product or products obtained in each case?
3. What are the products obtained during reduction of nitrobenzene, under different conditions?

4. How is benzene converted into nitrobenzene? Describe the details of the laboratory process. What are its properties and uses?
5. How will you convert :
 - (a) Nitrobenzene into *m*-dinitrobenzene
 - (b) Nitrobenzene into (i) Phenyl hydroxylamine (ii) Azoxybenzene, Azobenzene and Hydrazobenzene
 - (c) Nitrobenzene into aniline?
6. Write short notes on : (i) *m*-Dinitrobenzene, (ii) T.N.T.
7. Describe the laboratory preparation of nitrobenzene and give its properties and uses. (Panjab Inter 1961)
8. Outline a simple and direct scheme (indicating the reagent and conditions employed to convert :
 - (i) Nitrobenzene into azoxybenzene. (Panjab Inter 1960)
 - (ii) Nitrobenzene into (a) phenyl hydroxylamine (b) hydrazobenzene.
9. Starting from benzene, describe how would you get a pure sample of nitrobenzene? Give its important uses. (Panjab Inter 1954 S. 1949)
10. What happens when nitrobenzene is reduced in (a) Acidic solution (b) Neutral solution (c) Alkaline solution? (Panjab Inter 1952)
11. Write a note on T.N.T.
12. What do you understand by the term Nitration? How is nitration of phenol carried out? Give the utility of the operation. (Panjab Inter 1952)

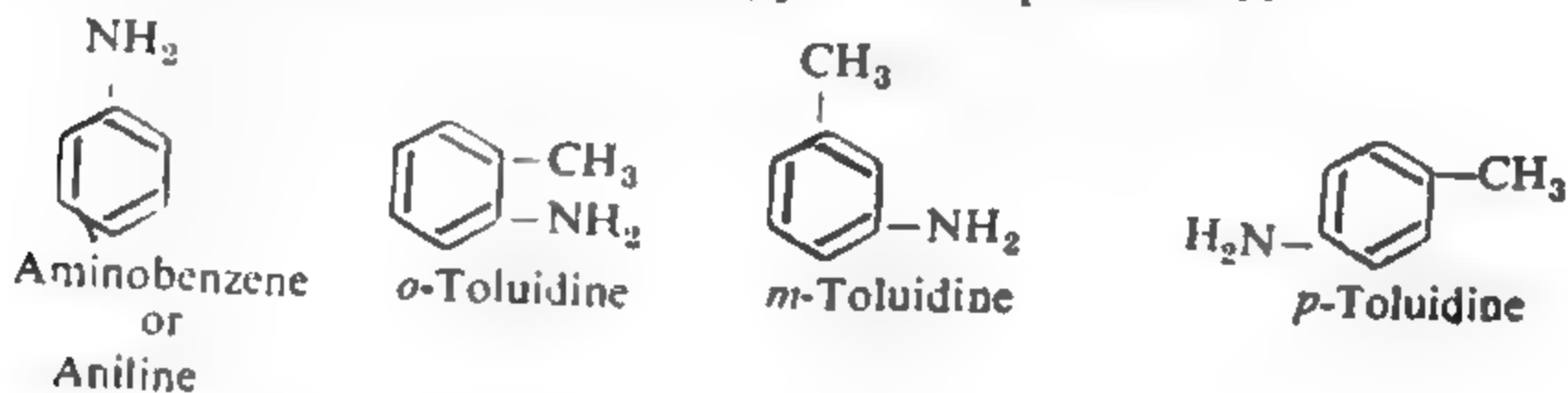
CHAPTER XLVIII

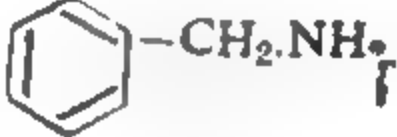
AROMATIC AMINO COMPOUNDS

Aromatic amino compounds, as stated earlier, are of two types :

(a) Those containing the amino (—NH_2) group or groups directly linked to the benzene nucleus, and

(b) Those containing amino-group linked to a carbon atom in the side-chain. Examples of the first type of compounds are :



Benzylamine  is an example of the second type,

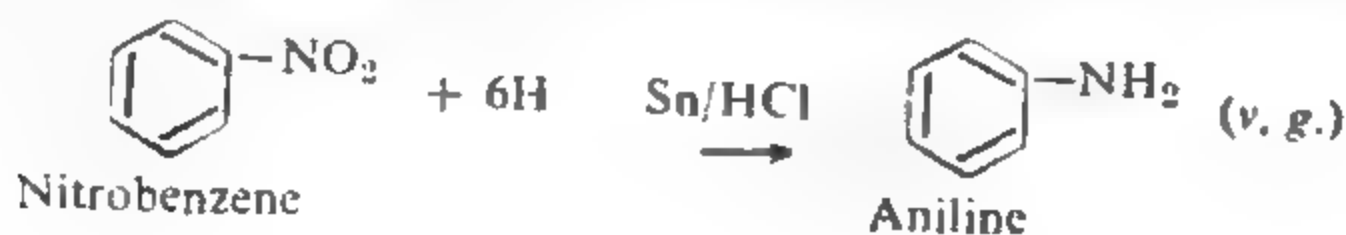
Aromatic amines may be primary, secondary or tertiary. For example, $\text{C}_6\text{H}_5\text{NH}_2$, aniline, is a primary amine whereas $\text{C}_6\text{H}_5\text{NHCH}_3$ methyl aniline (or phenyl methyl amine), and $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, dimethyl aniline (or dimethyl phenyl amine), are examples of secondary and tertiary amines respectively. Diphenyl amine ($\text{C}_6\text{H}_5\text{NH.C}_6\text{H}_5$) and triphenyl amine ($(\text{C}_6\text{H}_5)_3\text{N}$), are examples of pure aromatic secondary and tertiary amines.

ANILINE, PHENYLAMINE, AMINO BENZENE

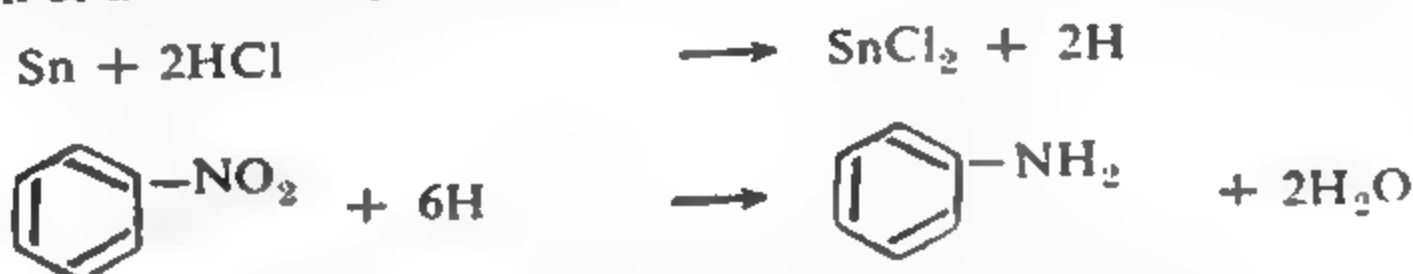


Aniline was first obtained by Unverdorben in 1826, by dry distillation of indigo and hence its name (Spanish : *anil*=Indigo). Runge (1834) discovered it in coal tar.

(1) **Laboratory Preparation** Aniline is conveniently prepared in the laboratory by the reduction of nitrobenzene with tin and hydrochloric acid.



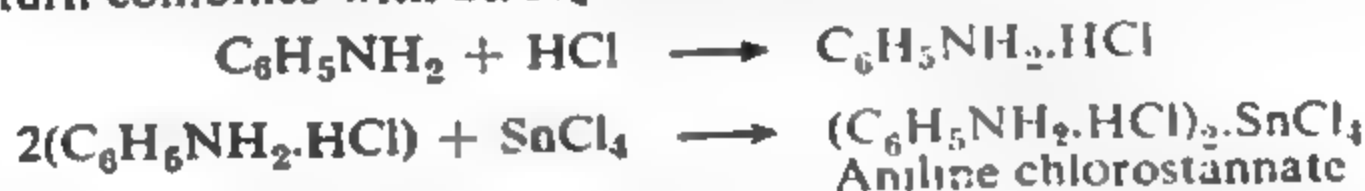
25 gm. of nitrobenzene and 50 gm. of granulated tin are placed in a 500 c.c. round bottomed flask fitted with a reflux condenser. 20 c.c. of concentrated hydrochloric acid are added through the condenser and the flask is shaken. A vigorous reaction takes place. When the reaction has subsided, another 20 c.c. of the acid are added and the flask shaken. If the reaction becomes very violent, generating much of heat, it is necessary to cool the flask under tap. This process is repeated until 100 c.c. of the acid have been added. The flask is then heated on a water bath, with occasional shaking, until the smell of nitrobenzene has vanished. The condenser is now removed and a strong solution of 75 gm. of caustic soda in about 100 c.c. of water is added. A white precipitate* is formed first which dissolves later on and aniline separates out as a dark oil. From this reaction mixture, aniline is separated by steam distillation. To the distillate some sodium chloride is added when aniline forms a distinct separate layer as it is far less soluble in sodium chloride solution than in water. The aniline is finally extracted with ether in a separating funnel. The solution of aniline in ether is kept overnight in contact with solid potassium hydroxide and distilled. Ether distils over at 34-35° and aniline at 180-184°. The reactions taking place during the preparation of aniline are given below :



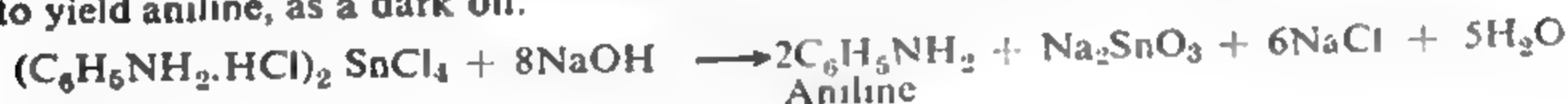
The stannous chloride formed also reduces nitrobenzene to aniline.



Aniline, being a base, combines with hydrochloric acid to form its hydrochloride, which in turn combines with SnCl_4 to form a double salt, aniline chlorostannate.

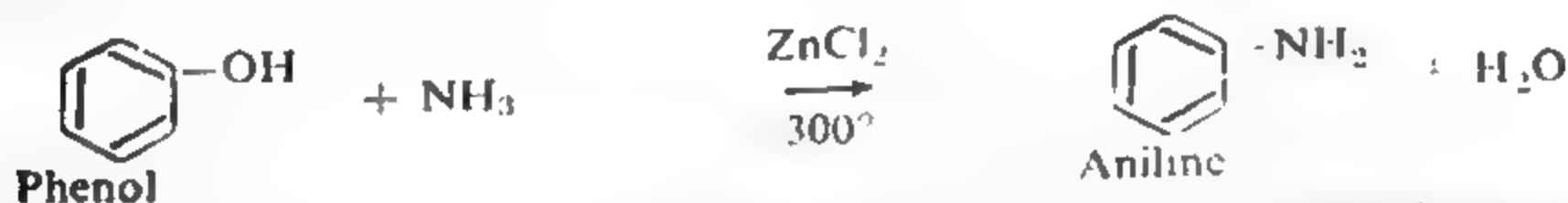


On addition of an excess of caustic soda, the aniline chloro-stannate decomposes to yield aniline, as a dark oil.



Aniline can also be prepared :

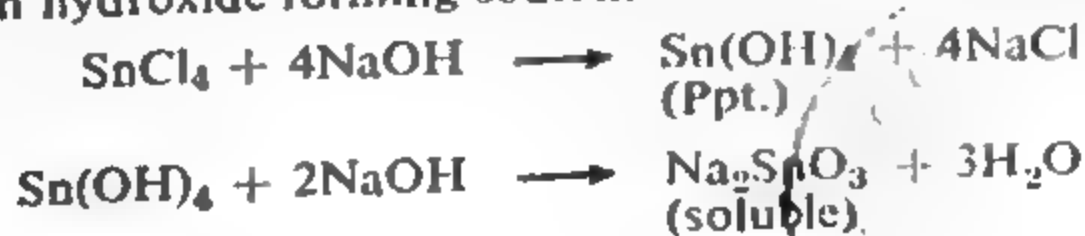
2. By heating phenol with ammonia at 300° under pressure, in the presence of zinc chloride.



3. By the action of bromine and aqueous or alcoholic potash on benzamide (*i.e.*, Hofmann's bromamide reaction).



*The white ppt. is due to the formation of stannic hydroxide, which dissolves in excess of sodium hydroxide forming sodium stannate.



4. Industrial Preparation. Aniline is prepared on an industrial scale :

(i) *By the reduction of nitrobenzene with scrap iron and concentrated hydrochloric acid.* Iron reacts with acid to produce nascent hydrogen which reduces nitrobenzene to aniline. The aniline obtained reacts with hydrochloric acid to form aniline hydrochloride ($C_6H_5NH_2 \cdot HCl$), which is decomposed by adding milk of lime. The liberated aniline is recovered by steam distillation (Fig. 1). The crude product is purified by distillation under reduced pressure.

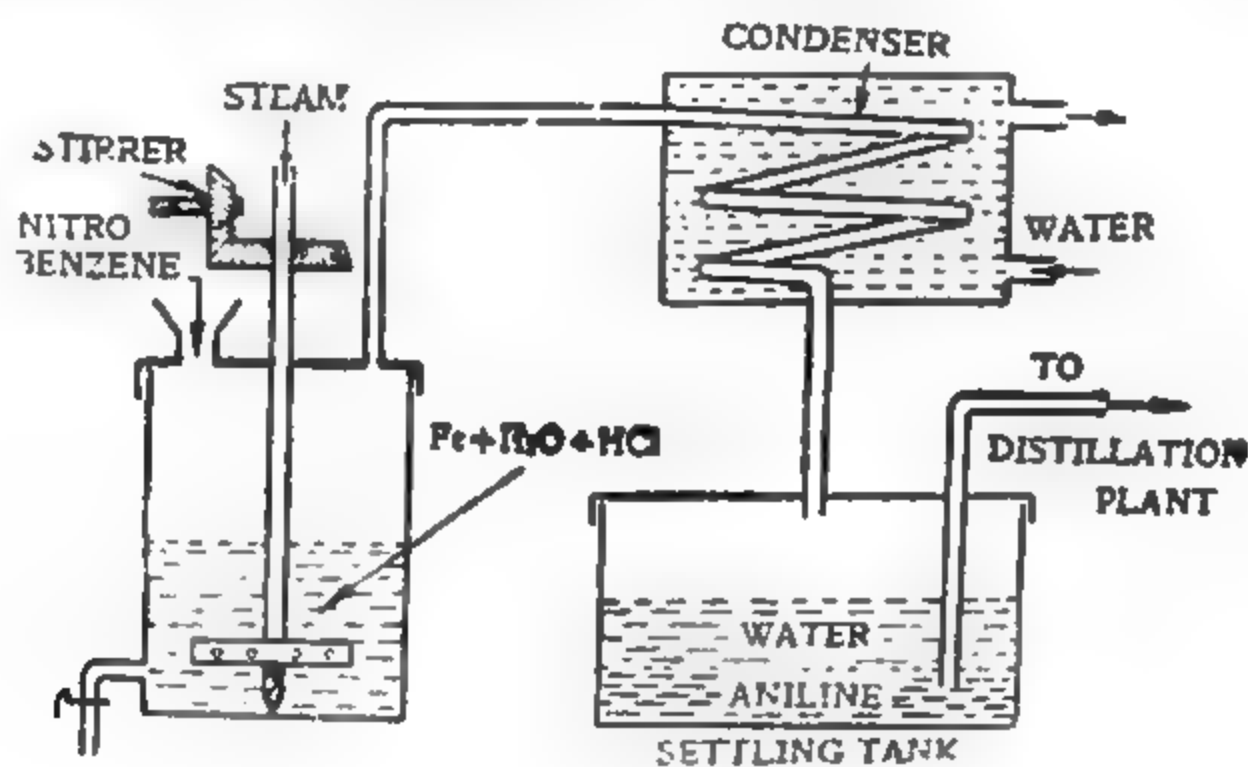
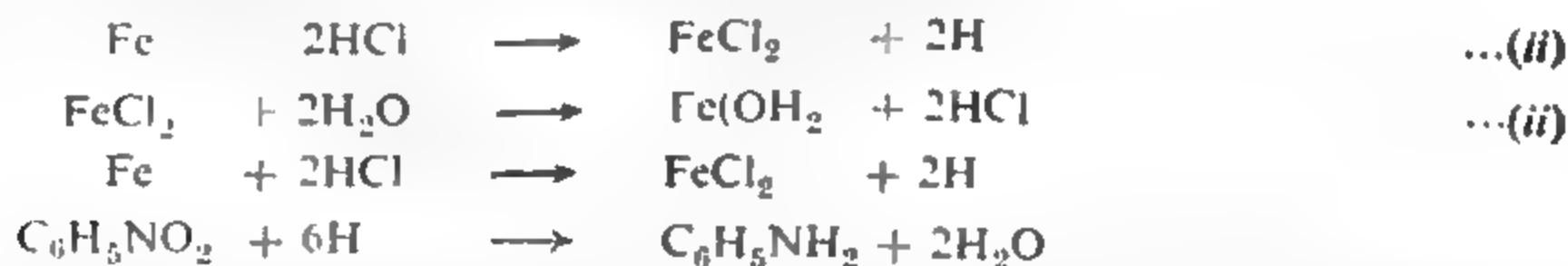


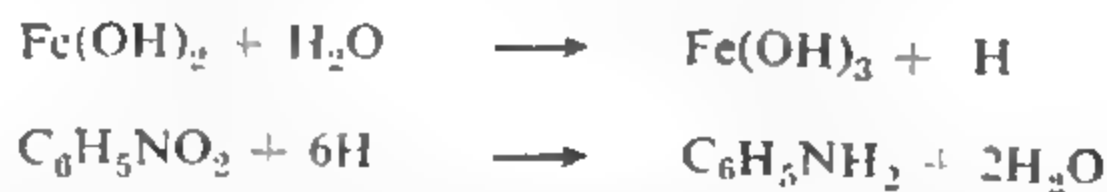
Fig. 1. Manufacture of aniline.

The reduction is supposed to take place in the following stages :

(i) Iron reacts with acid to form nascent hydrogen and ferrous chloride. The ferrous chloride reacts with water (which is also present in excess) to give ferrous hydroxide and hydrochloric acid, which, in turn, reacts with more of iron to produce more of nascent hydrogen, used for reducing nitrobenzene.



(ii) The ferrous hydroxide produced above may also act as a reducing agent, forming nascent hydrogen and ferric hydroxide, thus reducing a further quantity of nitrobenzene.



Obviously, the quantity of hydrochloric acid used up is much less than that required when nascent hydrogen is to be produced from iron and acid only.

Actually, only about 1/40th of the calculated quantity of hydrochloric acid is used.

(ii) Aniline is also manufactured from chlorobenzene by heating the latter with an excess of aqueous ammonia under pressure at 200°

in the presence of cuprous oxide.



Physical Properties. Freshly prepared aniline is a colourless oily liquid boiling at 184° , but darkens on exposure to light and air.* It has a characteristic unpleasant odour and is poisonous in nature. It is only slightly soluble in water, but dissolves readily in organic solvents. It is volatile in steam.

Chemical Properties. Aniline shows the characteristic behaviour of

(i) an amino group and (ii) benzene nucleus.

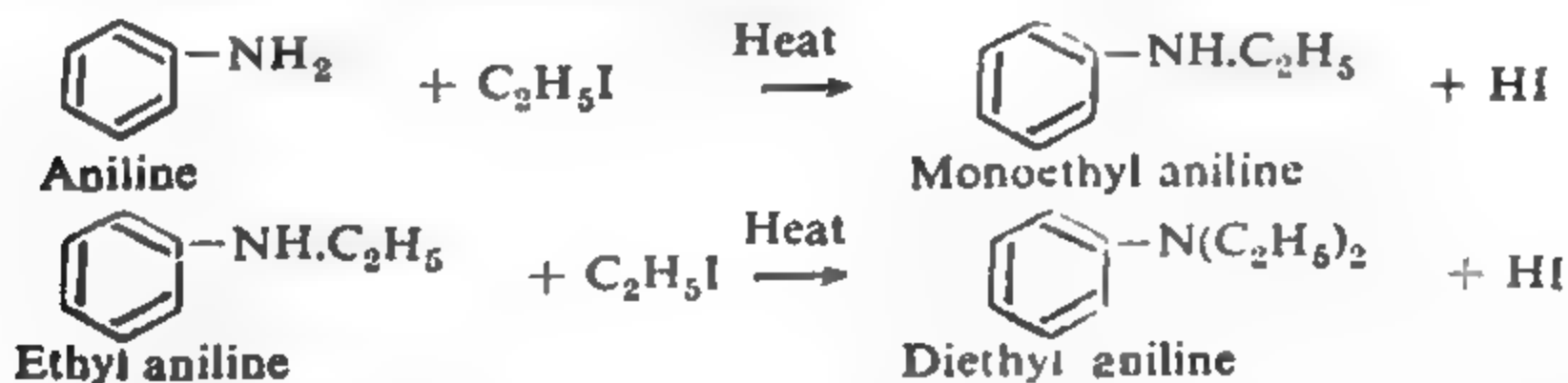
(i) **Reactions of the Amino Group.**

1. Basic character. Aniline is neutral to litmus, but combines with acids to form salts. For example, with hydrochloric acid and sulphuric acid it forms aniline hydrochloride and aniline sulphate respectively. Aniline behaves as a mono-acid base.

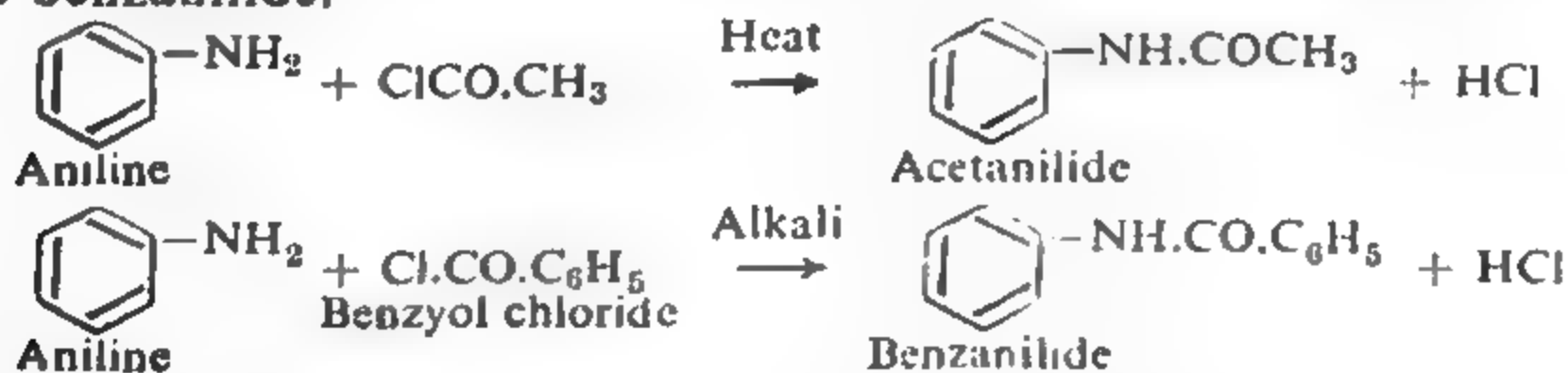


The salts are crystalline and soluble in water.

2. Alkylation. Aniline reacts with alkyl halides to give mono and dialkyl derivatives. For instance, with ethyl iodide, monoethyl and diethyl anilines are obtained.

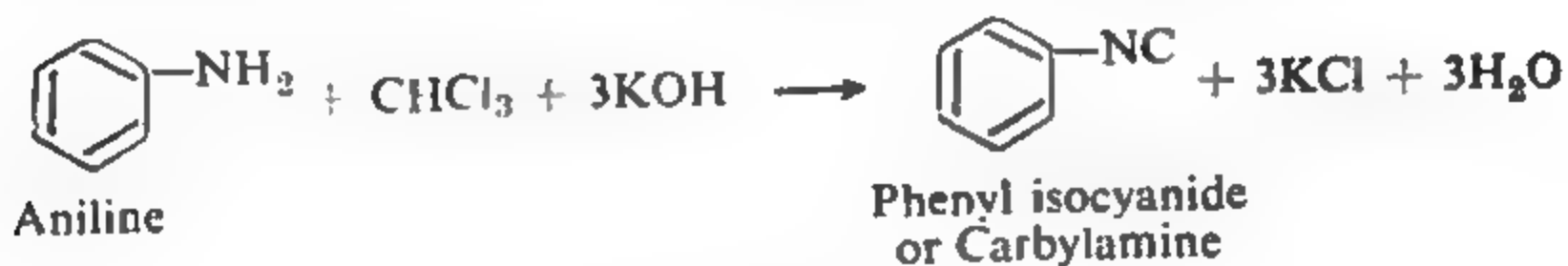


3. Acetylation and Benzoylation Aniline reacts with acetyl chloride or acetic anhydride forming *acetanilide*, and with benzoyl chloride to give *benzanilide*.

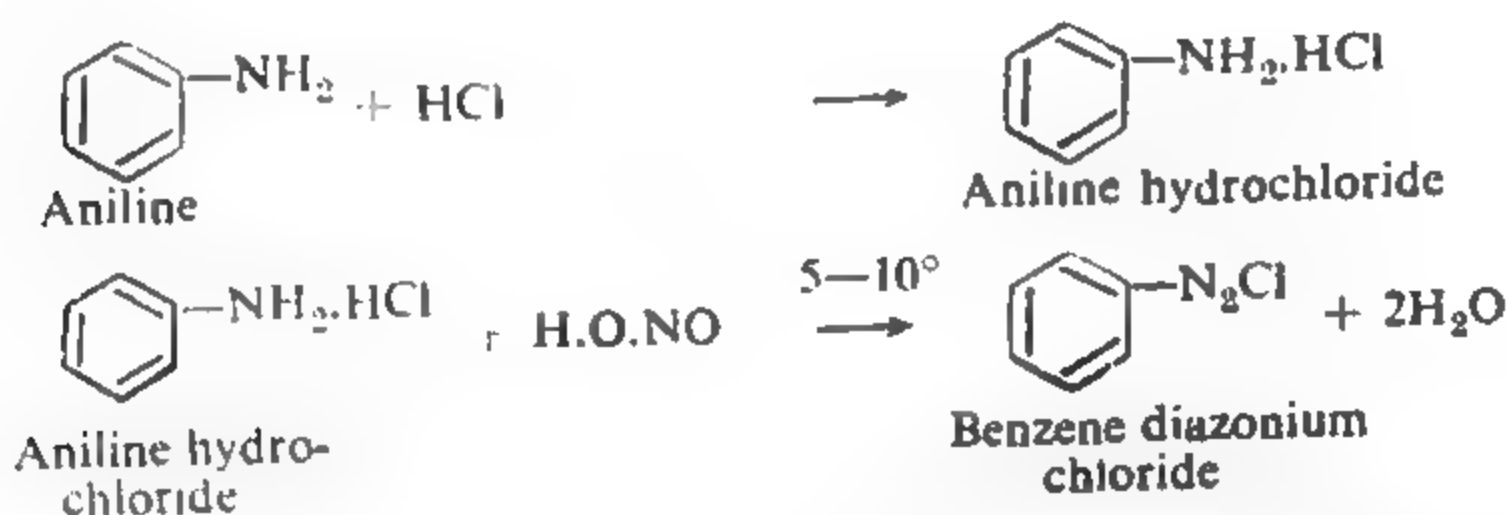


*The darkening of aniline is known to occur only when aniline is prepared from benzene obtained from coal tar, and does not occur if the benzene is obtained by another method (e.g., from acetylene). Therefore, darkening is probably due to the oxidation of thiophene which is almost always present as an impurity in benzene obtained from coal tar.

4. **Carbylamine reaction.** Aniline, when warmed with chloroform and alcoholic caustic potash, forms phenyl isocyanide (phenyl carbylamine), which is characterised by an extremely unpleasant odour.



5. **Diazotization.** Aniline dissolved in hydrochloric acid, reacts with nitrous acid (produced by the action of sodium nitrite and dilute hydrochloric acid) at a temperature between $5-10^\circ$, to form diazonium salt. Thus,

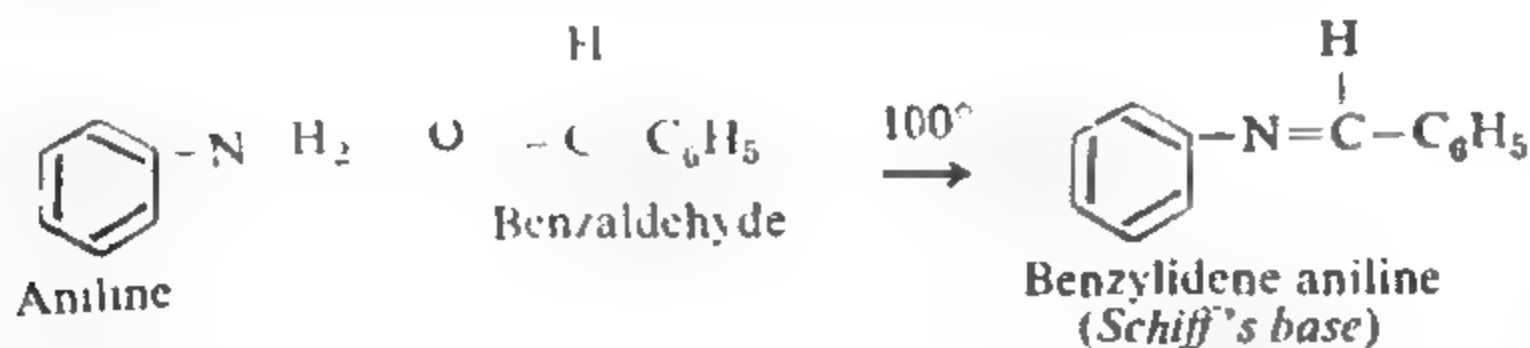


The diazonium salts are very important compounds since they are frequently used in organic synthetic work.

It is worth mentioning that aniline reacts with *hot* nitrous acid at about 50° in the same manner as the aliphatic amines, producing the corresponding hydroxy compound with the evolution of nitrogen.



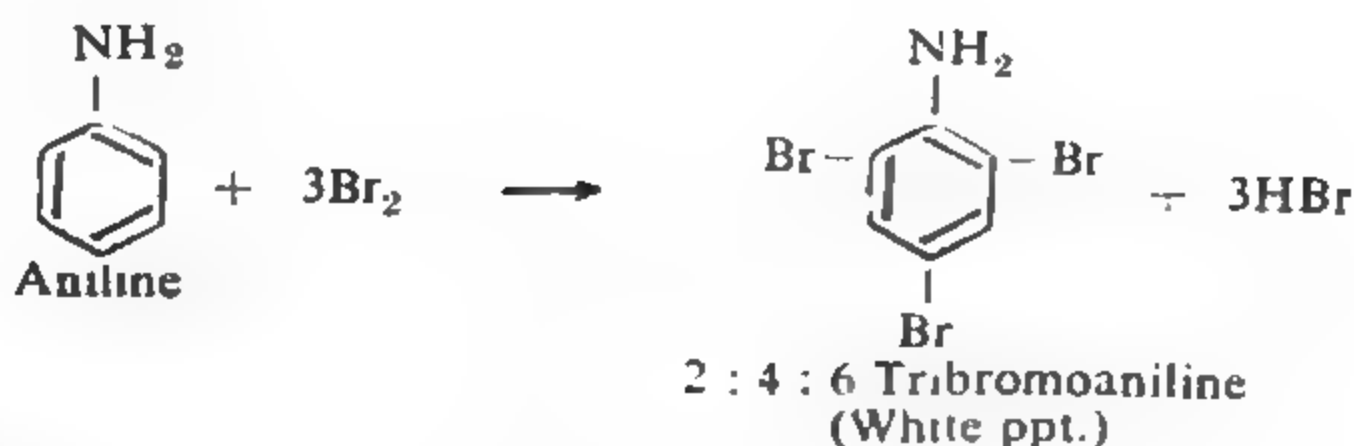
6. **Condensation with aldehydes.** Aniline condenses with aldehydes (equal volumes) on heating to form *anils* or *Schiff's base*.



(ii) Reactions of the Benzene Nucleus

1. **Halogenation.** Aniline undergoes halogenation much more readily than benzene to yield *o*- and *p*-substitution products (Crum Brown and Gibson's Rule). For instance, on addition of bromine water to an aqueous solution of aniline, a white precipitate of 2 : 4 : 6 tribromo-

aniline is obtained.

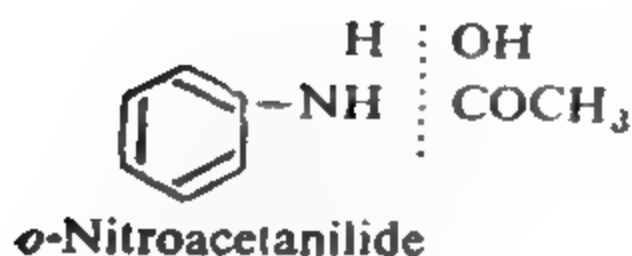
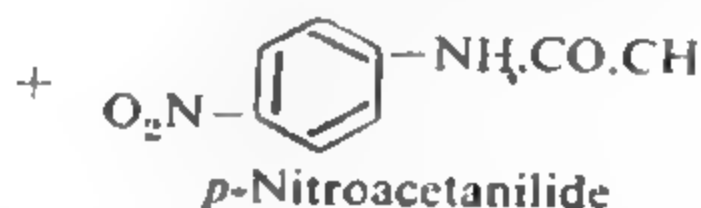
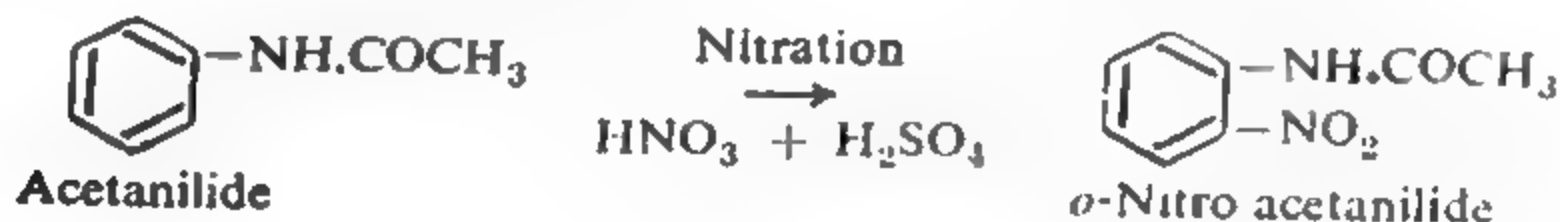


This reaction is almost instantaneous and is used as a test for aniline.

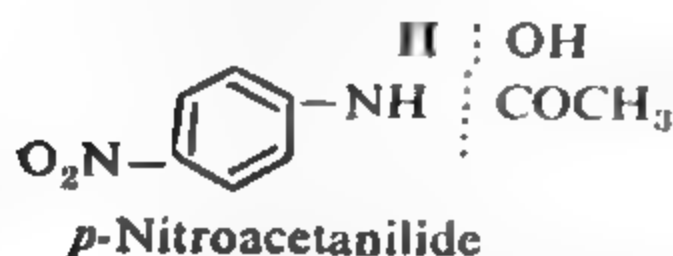
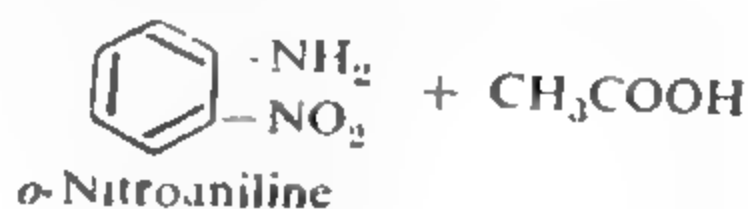
2. **Sulphonation.** Aniline, on heating with fuming sulphuric acid (sulphuric acid containing dissolved sulphur trioxide) at 180° , yields mainly sulphanilic acid (*p*-amino-benzene sulphonic acid).



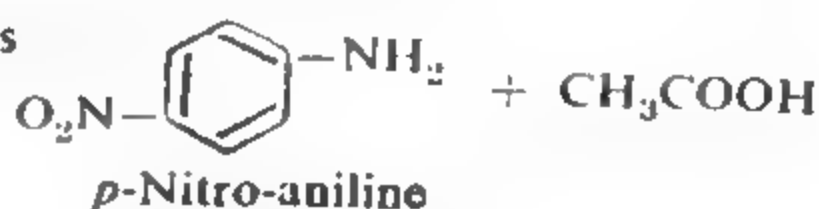
3. **Nitration.** The amino group is too easily susceptible to oxidation. Therefore, direct nitration is not possible. However, nitration can be effected indirectly by *protection of the amino group by acetylation*. The acetyl derivative is nitrated and the product hydrolysed with 70% sulphuric acid. Thus,



Hydrolysis

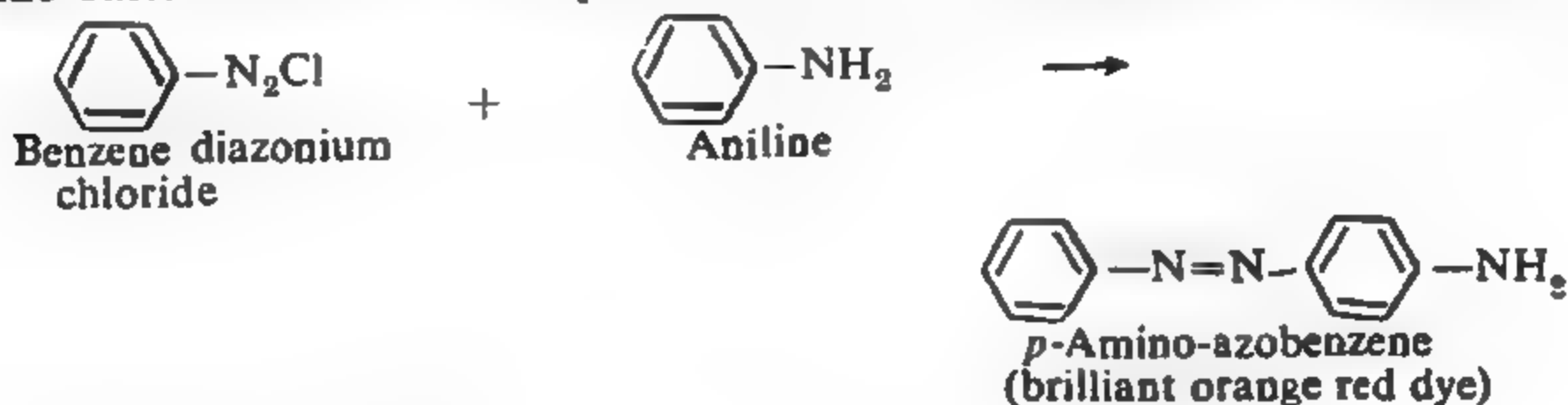


Hydrolysis



It is interesting to note that direct nitration is also possible provided a very large excess of sulphuric acid is present in the nitrating mixture. The product, however, under these conditions, is mainly *m*-nitro-aniline containing a little of the para isomer.

4. **Coupling with diazonium salts.** Aniline couples with aromatic diazo salts to form azo-compounds, which are brilliant orange-red dyes.



(ii) Other Reactions

Oxidation. Aniline is very readily oxidised, the products of oxidation depend upon the oxidising agent employed. For instance,

(a) with sodium dichromate and sulphuric acid under controlled conditions, aniline gives black solid, known as aniline black.

(b) prolonged oxidation of aniline with the above reagent yields benzoquinone, $\text{O}=\text{C} \begin{array}{c} \text{CH}=\text{CH} \\ \text{CH}=\text{CH} \end{array} \text{C}=\text{O}$.

(c) with bleaching powder or sodium hypochlorite, a purple coloured compound is obtained.

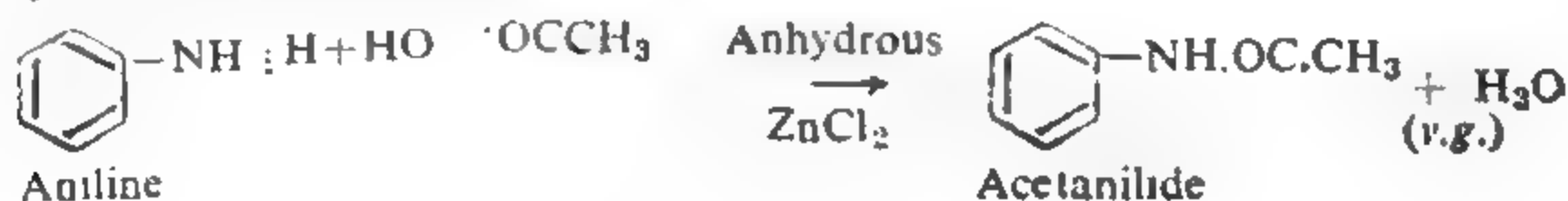
Uses. Aniline is an important intermediate in the manufacture of dyes and drugs. It is also used as an accelerator in vulcanisation of rubber.

Tests Aniline can be detected by the following tests :

1. Aniline gives carbylamine reaction.
2. A small amount of aniline is dissolved in excess of dilute hydrochloric acid and cooled in ice. To this is added an ice-cold solution of sodium nitrite, till a drop of the reaction mixture gives a blue colour with starch iodide paper. This solution is then added to a solution of β -naphthol in sodium hydroxide. A brilliant red dye is formed.
3. A little of bromine water is added to some aniline in a test-tube. On shaking, a white ppt. of tribromo-aniline is obtained.
4. A few drops of a solution of bleaching powder, when added to a water-aniline mixture, produces a purple coloration, which quickly turns brown.
5. Ferric chloride when added to a solution of aniline in dilute hydrochloric acid produces a pale green coloration.

Acetanilide, Antifebrin, $\text{C}_6\text{H}_5\text{NH.CO.CH}_3$

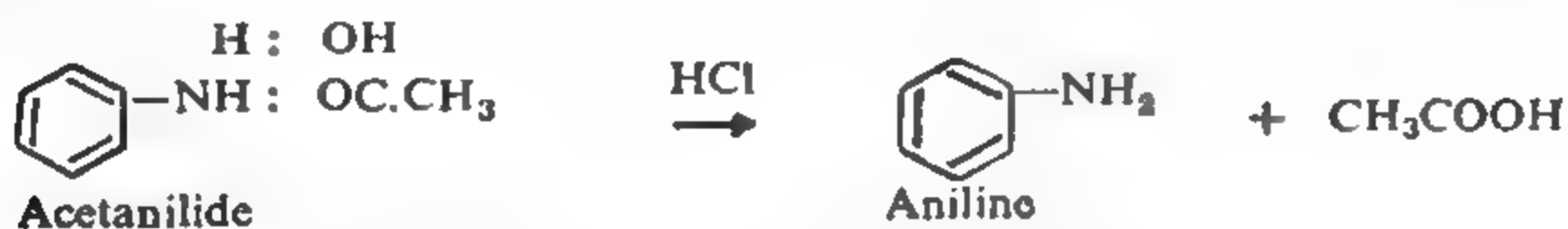
Acetanilide is prepared by acetylating aniline with acetyl chloride or better with acetic anhydride. It is conveniently prepared in the laboratory by refluxing aniline with glacial acetic acid in the presence of anhydrous zinc chloride.



The hot reaction mixture is poured into cold water when crude acetanilide crystals separate out. These are dissolved in water, heated with animal charcoal, filtered and recrystallised.

Properties. Acetanilide is a colourless crystalline compound melting at 114° . It is sparingly soluble in cold water, but dissolves readily in hot water.

On boiling with a dilute mineral acid or an aqueous solution of alkali, acetanilide undergoes hydrolysis producing aniline and acetic acid.



Uses. It is used for relieving headache and as an antipyretic, that is, for lowering the temperature of the body, under the name '*antifebrin*'.

Benzylamine, Phenyl methylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

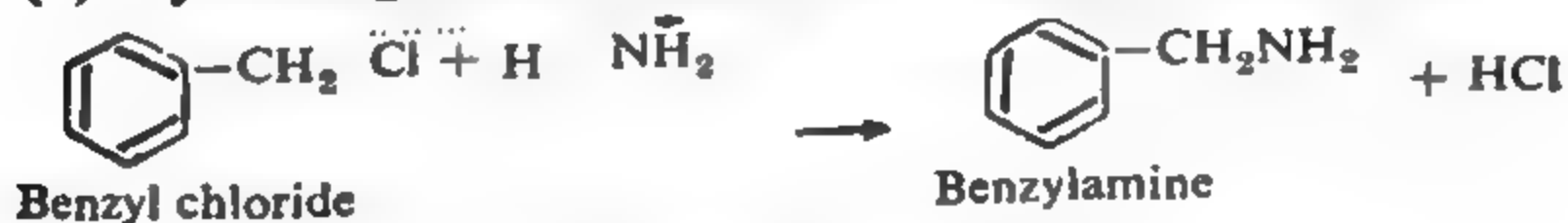
Benzylamine is a typical aromatic amine, containing the amino-group in the side chain. It resembles aliphatic amines in its methods of preparation and properties.

Preparation. Benzylamine may be prepared by the following methods :

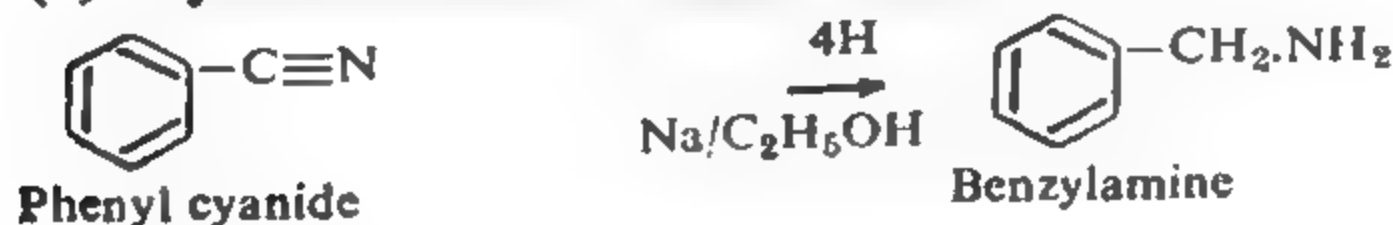
(1) **By Hofmann's bromamide reaction.** Phenyl acetamide, $\text{C}_6\text{H}_5\text{CH}_2\text{CONH}_2$, is treated with bromine and potassium hydroxide to give benzyl amine.



(2) **By heating benzyl chloride with ammonia under pressure.**



(3) **By the reduction of phenyl cyanide.**

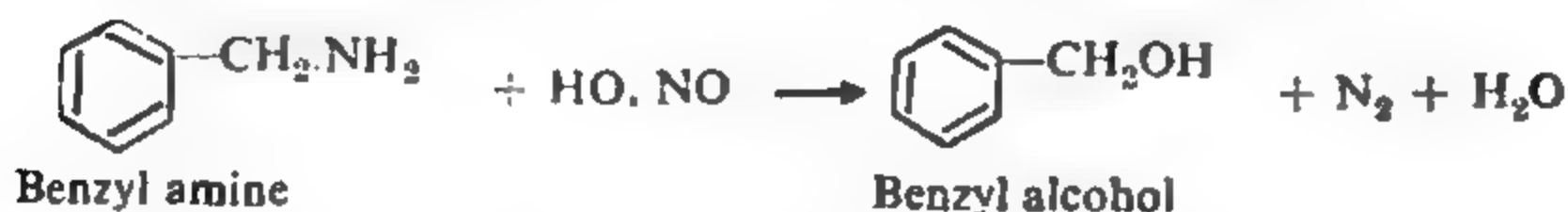


(4) **By heating benzyl alcohol with ammonia under pressure.**

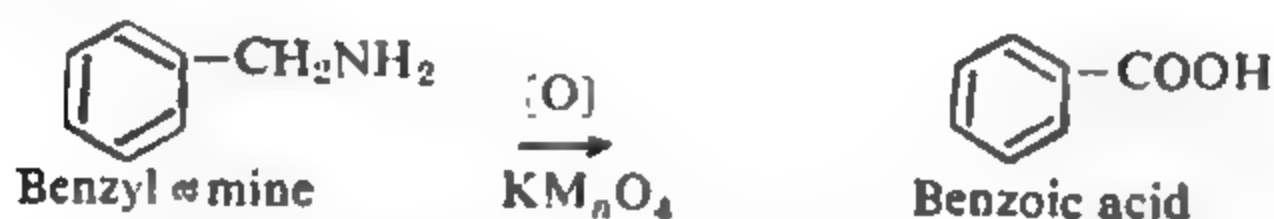


Properties. Benzylamine is a colourless liquid (b.p. 185°) with a characteristic ammoniacal smell. It is soluble in water and the solution is alkaline to litmus. Thus, it is more basic than aniline.

Chemically, benzylamine resembles the aliphatic amines and can be regarded as phenyl substituted methylamine. For example, with nitrous acid, it yields the corresponding alcohol (difference from aniline).



In addition, it shows the characteristic behaviour of the benzene nucleus. For instance, on oxidation with potassium permanganate, it gives benzoic acid.



Comparison of Aniline with Aliphatic Primary Amines

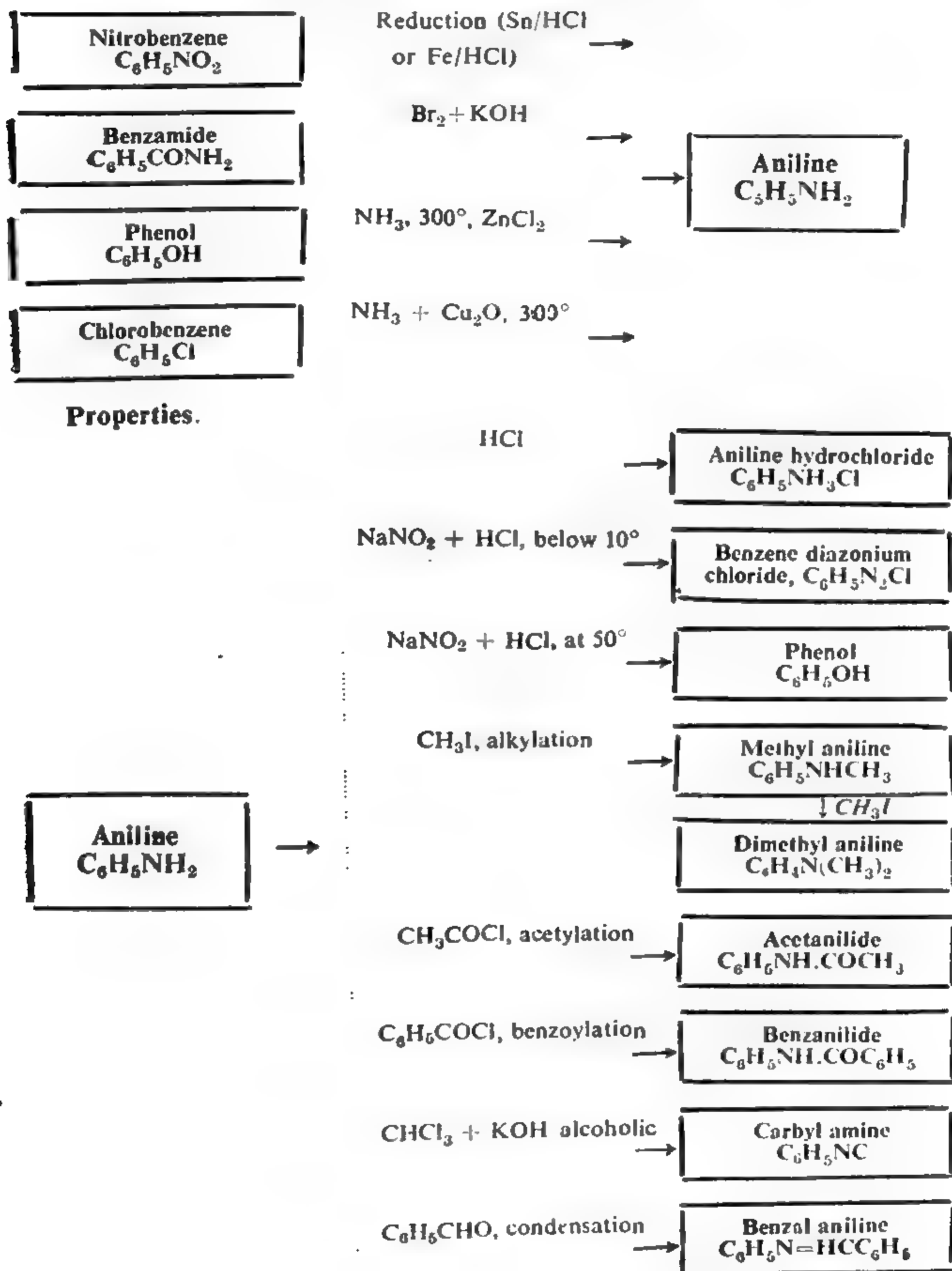
Common Properties

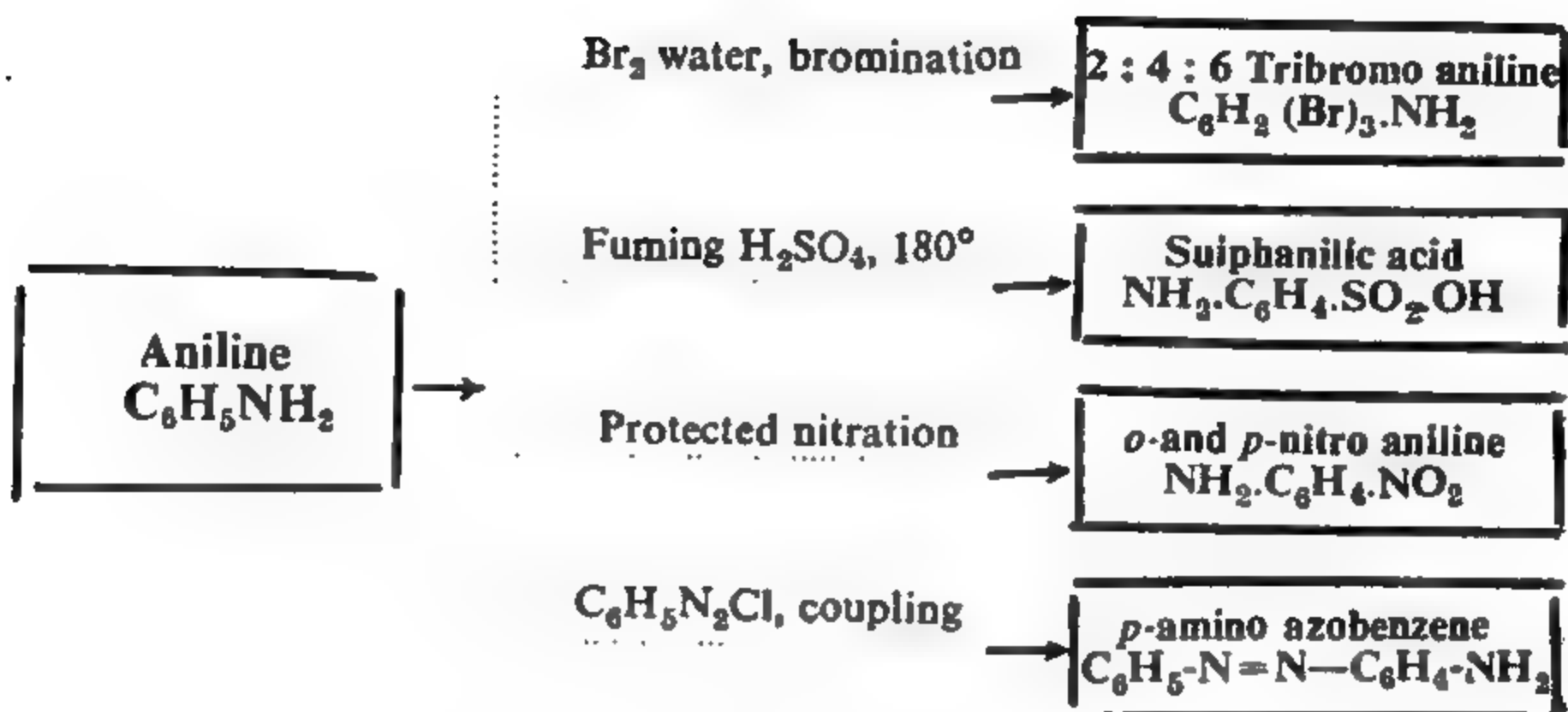
1. Both aniline and primary aliphatic amines give carbylamine reaction.
2. Both react with acids to form salts.
3. Both can be alkylated at the --NH_2 group to give secondary and tertiary amines.
4. Both can be acylated to form substituted amides.

Different Properties

1. Aniline is only sparingly soluble in water and its solution is *neutral* towards litmus. Aliphatic amines, on the other hand, are freely soluble in water and their solutions are *alkaline*.
2. Aniline reacts with HNO_2 ($\text{NaNO}_2 + \text{HCl}$) to give *diazonium* salt at low temperatures and *phenol* at high temperatures. Aliphatic amines give *alcohols* even at ordinary temperatures.
3. Aniline is readily oxidised giving different products under different conditions. Aliphatic amines are resistant towards oxidation.
4. Aniline, being an aromatic compound, permits halogenation, nitration and sulphonation in the nucleus. Aliphatic amines do not permit substitution in the hydrocarbon part.

SUMMARY OF A TYPICAL MEMBER PREPARATION AND PROPERTIES OF ANILINE





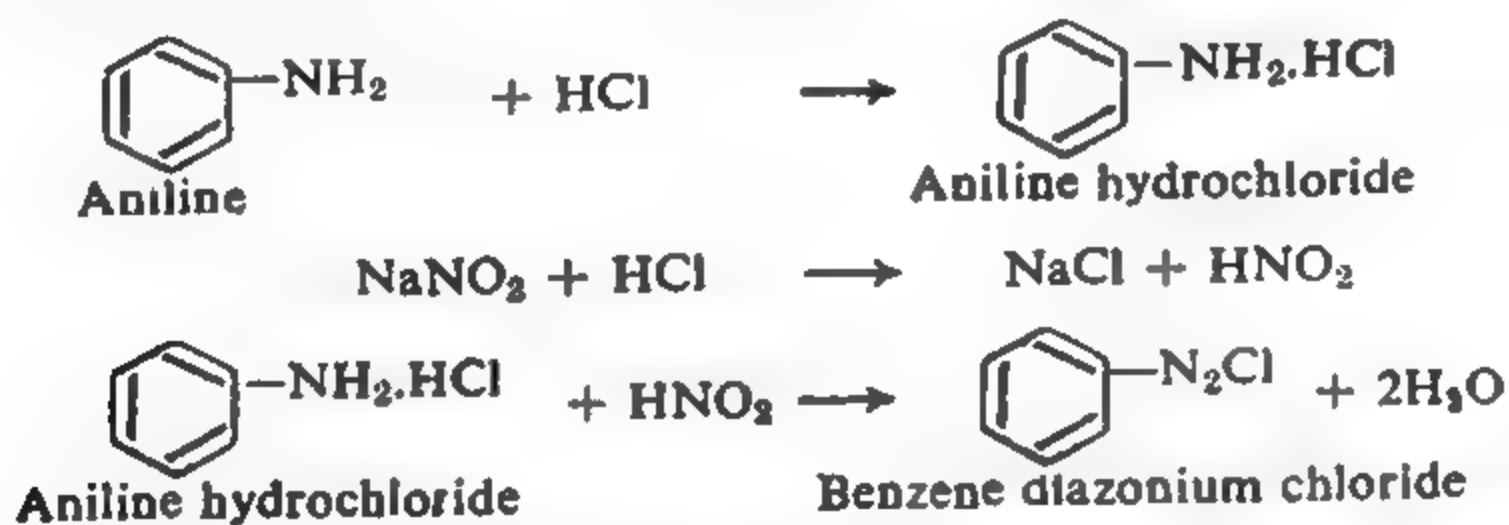
QUESTIONS

1. What are aromatic amino compounds and aromatic amines? How do they differ from each other? Exemplify your answer?
2. How will you prepare aniline in the laboratory? How will you convert aniline into (a) phenol (b) benzene (c) acetanilide (d) sulphanilic acid?
3. Give the preparation, properties and uses, if any, of (a) acetanilide (b) benzylamine.
4. Ethylamine and aniline are derivatives of ammonia. Bring out their similarities and dissimilarities in a tabular form. Illustrate your answer with equations where possible.
(Patna Inter 1959)
5. Describe the preparation, properties and uses of aniline. (Banaras Inter 1953)
6. How would you prepare a pure sample of aniline in the laboratory? Mention its important properties and tests you would apply to identify the substance.
(Jammu and Kashmir Inter 1953)
7. Describe the laboratory preparation of aniline and draw a neat labelled sketch of the apparatus used. In what respects does it differ from ethylamine? How does ethylamine react with (a) nitrous acid (b) acetyl chloride and (c) ethyl iodide?
(Banaras Inter 1957)
8. (a) Give the preparation, properties and uses of acetanilide.
(Panjab Inter 1961, 1960 S part)
(b) How will you obtain *p*-nitro aniline from aniline?
(Panjab Inter 1960, 1959 S)
9. In what chemical properties does an aromatic amine such as aniline differ from an aliphatic amine such as methylamine? Give chemical equations and name the products produced in each case.
(Panjab Inter 1958)
10. Write equations with conditions for reactions by which aniline forms (1) benzanilide (2) phenol (3) *p*-nitro-aniline.
(Panjab Inter 1956 part)
11. (a) Write a note on 'antifebrin'.
(Panjab Inter 1955 S part)
(b) Explain giving equations, where possible, what happens when chlorine is passed into aniline suspended in sodium hydroxide solution. (Panjab Inter 1953 part)
12. In the reduction of nitrobenzene with tin and hydrochloric acid, the final compound is aniline stannichloride. (C₆H₅NH₂HCl).SnCl₄. Write out practical method for the recovery of pure aniline from this compound. What is the action on aniline of (a) bromine water (b) a solution of bleaching powder (c) a solution of potassium dichromate in sulphuric acid and (d) nitrous acid? (Panjab Inter 1951 S)

CHAPTER II

DIAZO COMPOUNDS

Diazotisation. Aniline when treated with sodium nitrite and hydrochloric acid at temperatures below 10° gives *benzene diazonium chloride*. The reaction may be represented as below :



The process of the conversion of an aromatic amino compound into a diazonium salt is known as **diazotisation** or a **diazo reaction**.

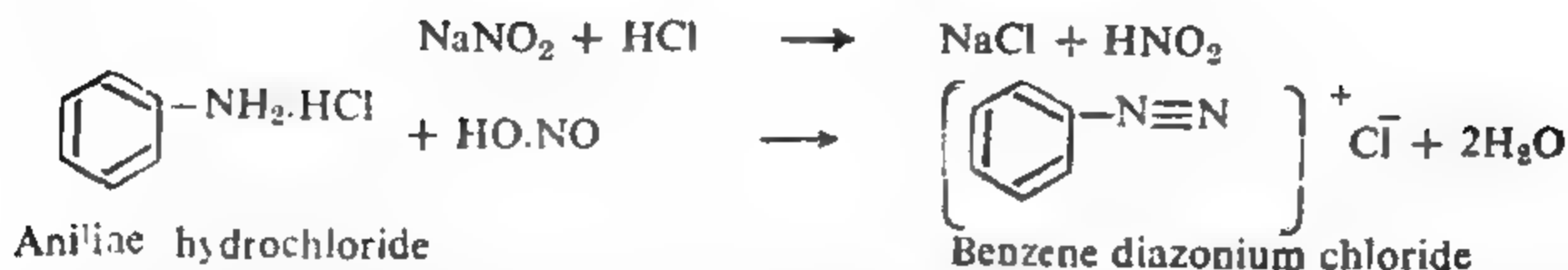
The name diazonium salt implies that the compound contains two nitrogen atoms and that it resembles ammonium salts (*di*=two, *azo*=nitrogen in French, *onium* is suffix from ammonium). These compounds are believed to have the structure $\left[\text{C}_6\text{H}_5\text{N}_2 \right]^+ \text{X}^-$

where X is any monovalent acid radical.

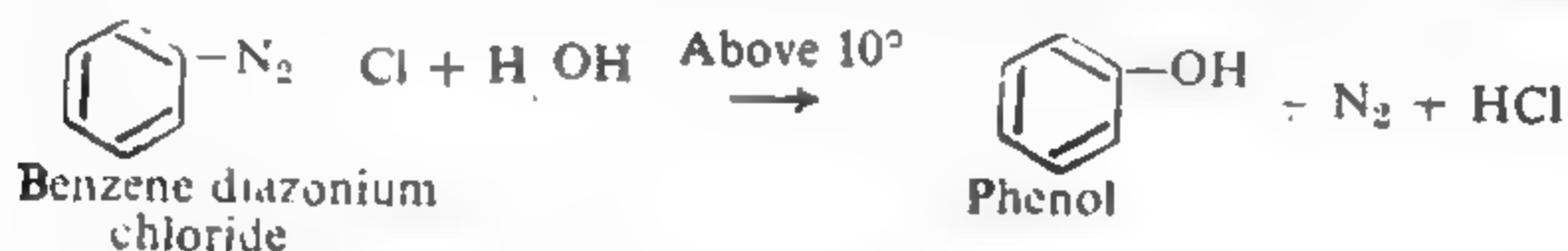
The diazonium salts are extremely reactive compounds. They occupy a unique position in aromatic chemistry, only comparable to that of alkyl halides on the aliphatic side. The diazo-compounds have an additional advantage over other organic synthetic reagents in being soluble in water. They are employed in the preparation of a large number of dye-stuffs and drugs.

BENZENE DIAZONIUM CHLORIDE, $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$

Laboratory Preparation. Benzene diazonium chloride is conveniently prepared in the laboratory by adding an aqueous solution of sodium nitrite to a solution of aniline in an excess of dilute hydrochloric acid.



The quantity of acid must be enough (i) to react with sodium nitrite or liberate nitrous acid and (ii) to keep the solution acidic so that aniline is present as aniline hydrochloride throughout the reaction. The quantity of sodium nitrite added must be slightly in excess of the calculated amount. The temperature must be maintained below 10° because above 10° , the benzene diazonium chloride reacts with water to produce phenol.



Practical Details. 15 c.c. of aniline are dissolved in 40 c.c. of concentrated hydrochloric acid diluted with its own volume of water in a 250 c.c. conical flask. This flask is kept in ice-cold water for some time. A solution of 62.5 gm. of sodium nitrite in about 30 c.c. of water is also kept in ice. When sufficiently cooled, the solution is added, in small quantities at a time, to the flask and the contents are shaken occasionally. The addition of sodium nitrite solution is continued till a drop of the reaction mixture turns starch iodide paper blue, showing the presence of free nitrous acid. The solution of the reaction mixture at this stage, contains benzene diazonium chloride, which is normally used as such for synthetic work.

The reaction is exothermic and, therefore, the containing vessel is kept in ice-cold water.

When needed on an industrial scale, benzene diazonium chloride or any other diazonium salt is manufactured in the same manner as above, with the only difference that larger quantities of the reagents are taken.

Physical Properties. Benzene diazonium chloride is a colourless crystalline solid, which turns dark on exposure. It is highly soluble in water but only sparingly so in alcohol and ether. Its aqueous solution conducts electricity. When dry, it is highly explosive.

Chemical Properties. Benzene diazonium chloride, as pointed out earlier, is a highly reactive compound. It undergoes a large number of reactions producing a large variety of aromatic compounds. Its reactions are of two types :

(i) Those in which the $-\text{N}_2\text{Cl}$ group is replaced by other monovalent atoms or groups evolving nitrogen and

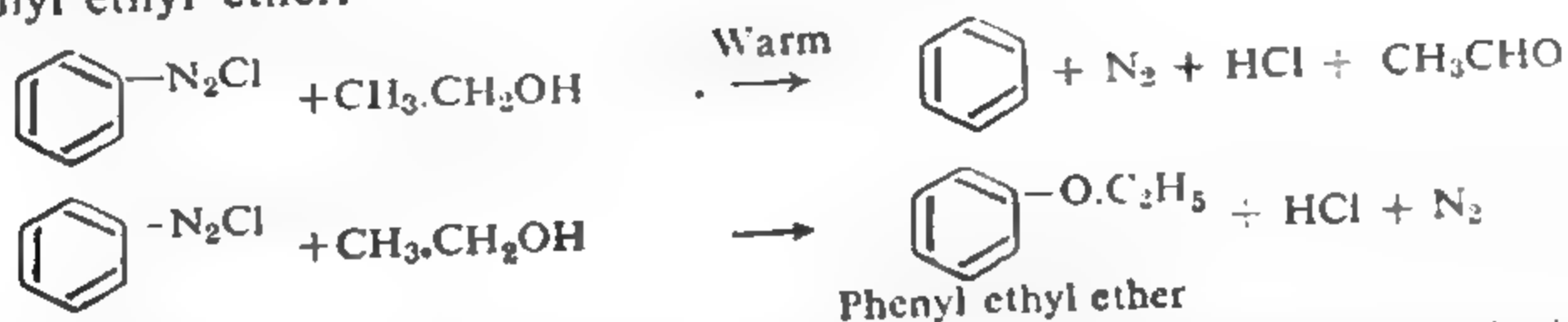
(ii) Those in which the nitrogen atoms are retained.

(i) Replacement reactions in which nitrogen is evolved.

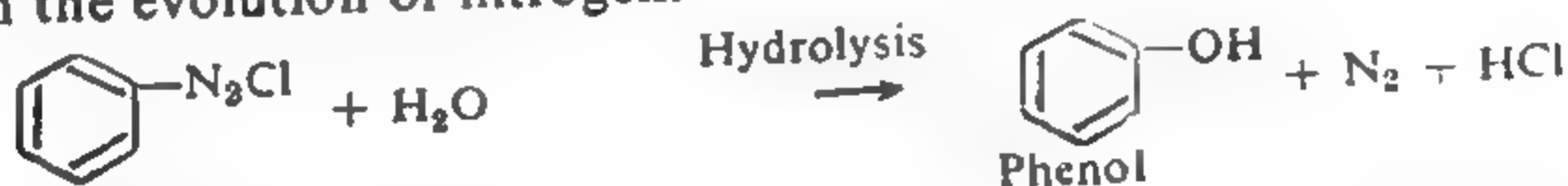
(1) Reduction in alkaline medium. When treated with sodium stannite solution, benzene diazonium chloride is reduced to benzene.



(2) **Reduction with alcohol.** When treated with ethyl alcohol, a part of the diazonium salt is reduced to benzene and the rest is converted into phenyl ethyl ether.

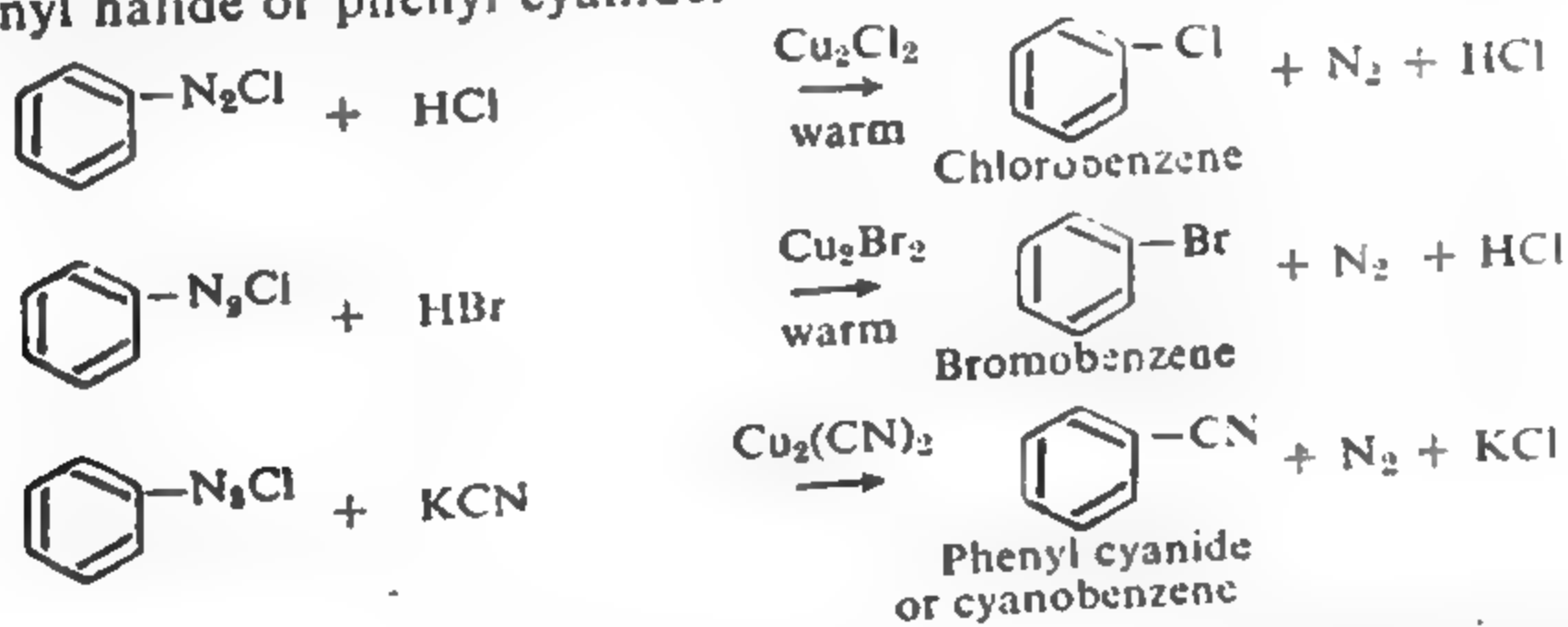


(3) **Hydrolysis.** An aqueous solution of benzene diazonium chloride when warmed cautiously to $50-55^\circ$, undergoes hydrolysis yielding phenol, with the evolution of nitrogen.

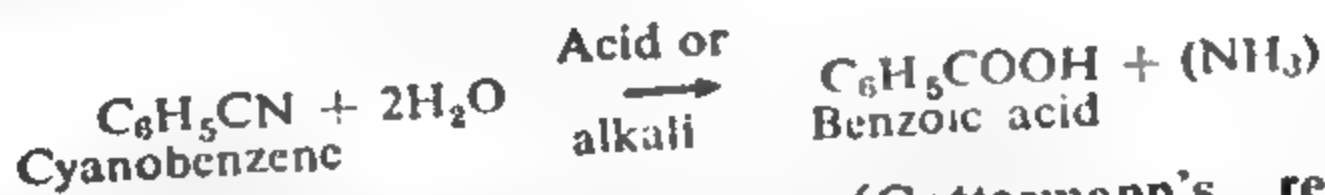


Phenol is recovered by steam distillation.

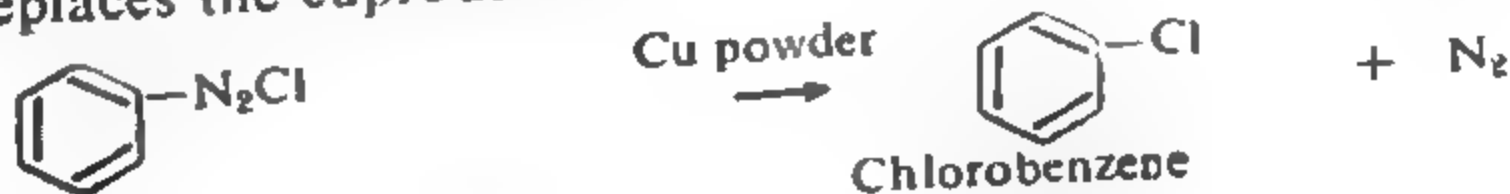
4. **Reaction with certain cuprous salts (Sandmeyer's reaction).** When a solution of benzene diazonium chloride is slowly run into a warm solution of (i) cuprous chloride in hydrochloric acid or (ii) cuprous bromide in hydrobromic acid or (iii) cuprous cyanide dissolved in potassium cyanide, the $-\text{N}_2\text{Cl}$ group is replaced by chlorine, or bromine or a cyanogen group resulting in the formation of the corresponding phenyl halide or phenyl cyanide.



Cyanobenzene may be hydrolysed by acid or alkali to give benzoic acid.



(5) **Reaction with finely divided copper (Gattermann's reaction)** The reaction is just a modification of the Sandmeyer's reaction, where copper powder replaces the cuprous salt.



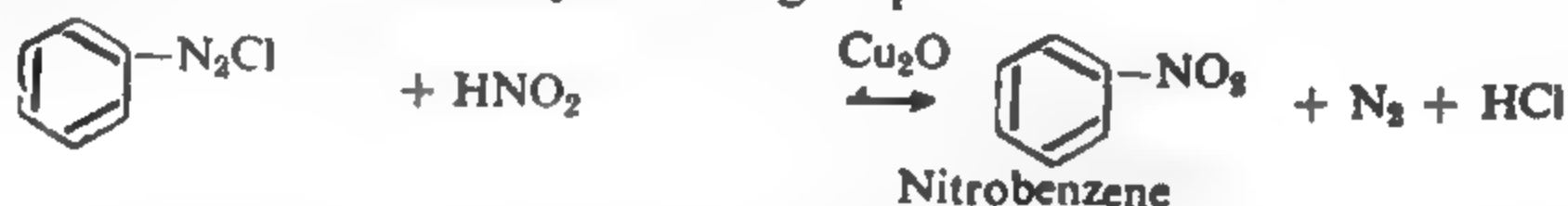
For getting bromobenzene, the starting material is benzene diazonium bromide.

6. **Reaction with potassium iodide.** When an aqueous solution of potassium iodide is slowly added to a cold solution of benzene diazonium chloride, a vigorous reaction occurs with the evolution of nitrogen and iodobenzene is formed.



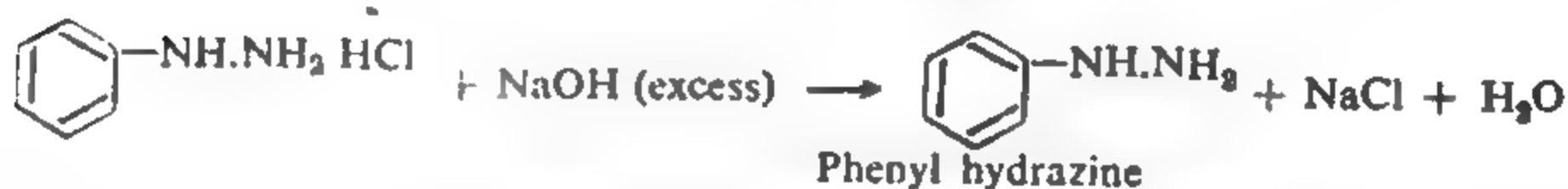
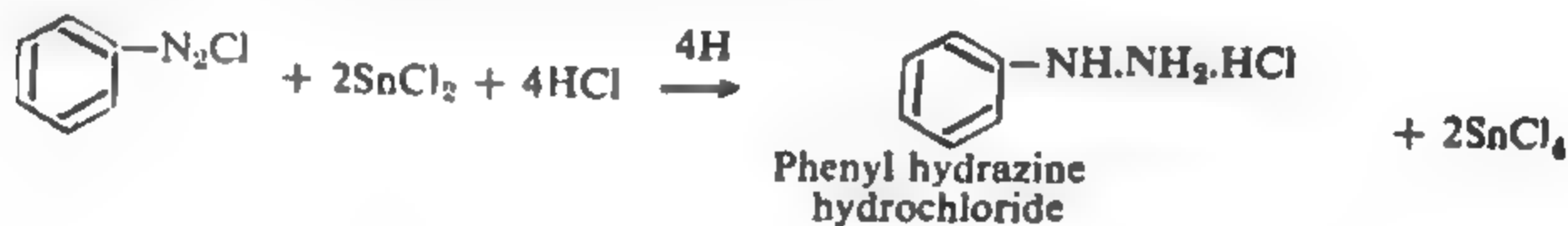
This reaction is of particular importance as it places at our disposal a very convenient method of introducing the iodine atom into the benzene ring.

7. **Reaction with nitrous acid.** When benzene diazonium chloride is treated with nitrous acid in the presence of cuprous oxide, the diazo group (N_2Cl) is replaced by a nitro group.



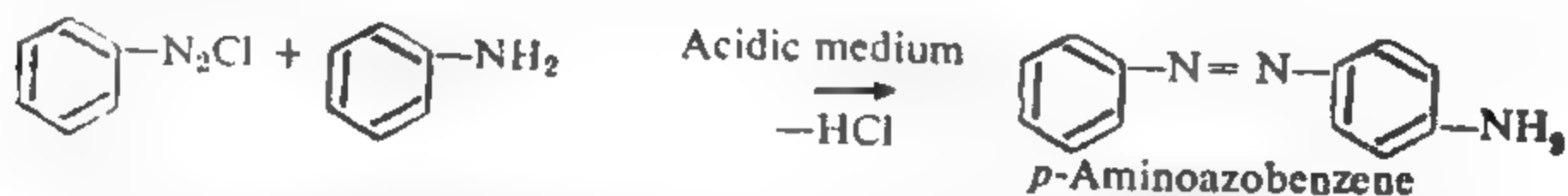
(ii) **Reactions in which the nitrogen atoms are retained.**

1. **Reaction with acidic stannous chloride.** Benzene diazonium chloride gets reduced with a solution of stannous chloride in concentrated hydrochloric acid to produce a precipitate of phenyl hydrazine hydrochloride, from which phenyl hydrazine can be obtained by the addition of an excess of sodium hydroxide solution.

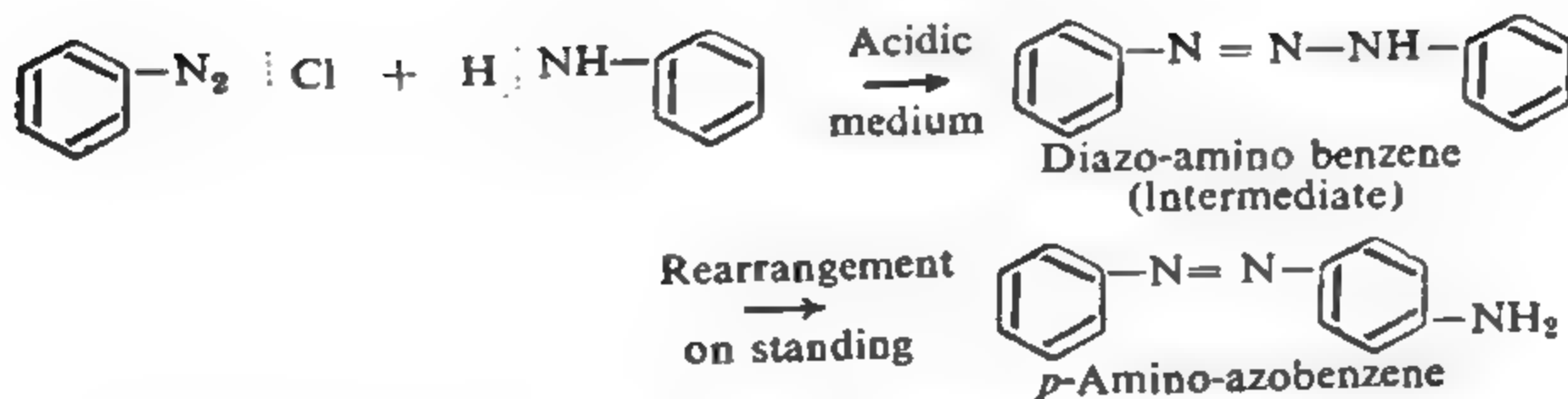


2. **Condensation reactions with aromatic amino compounds or phenols (Coupling reactions).**

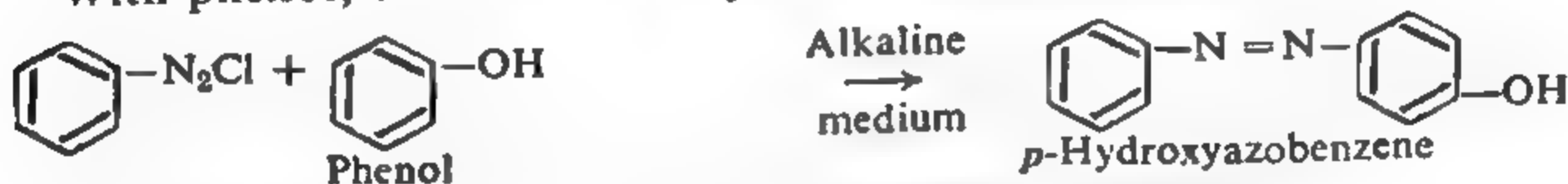
Benzene diazonium chloride reacts with aromatic amino compounds in slightly acidic medium and with phenols in slightly alkaline medium to give *azo dyes*.



The above reaction is supposed to take place in two steps : the diazo-amino benzene first formed rearranges itself into an azo compound.



With phenol, the reaction may be depicted as below :



The above reactions are known as **Coupling reactions**.

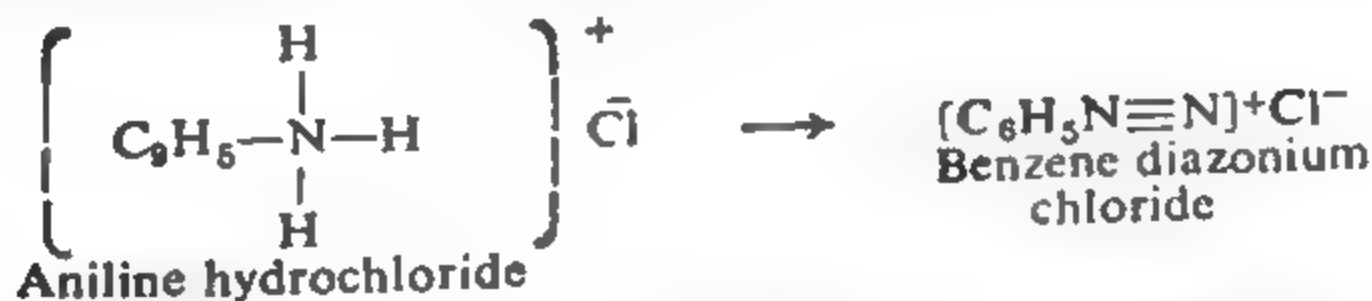
Both the above compounds, *viz.*, *p*-aminoazobenzene and *p*-hydroxyazobenzene are typical members of brilliant coloured dyes called **azo-dyes**.

Uses. (1) Benzene diazonium chloride is a very useful synthetic reagent and can be used to yield a large variety of aromatic compounds, *viz.*, hydrocarbons, ethers, halogen derivatives, nitro derivatives, etc.

(2) It is used for the preparation of phenyl hydrazine and azo dyes.

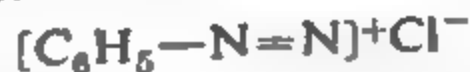
(3) It is employed in calico-printing.

Structure of Benzene Diazonium Chloride. Benzene diazonium chloride is a salt with a structure analogous to that of ammonium chloride and is derived from aniline hydrochloride by substituting a nitrogen atom for three hydrogen atoms.



This representation is supported by the fact that the solubility and conductivity of benzene diazonium chloride in its aqueous solution is of the same order as that of ammonium chloride.

However, formation of azo-compounds or phenyl hydrazine hydrochloride suggests an alternative structure represented as



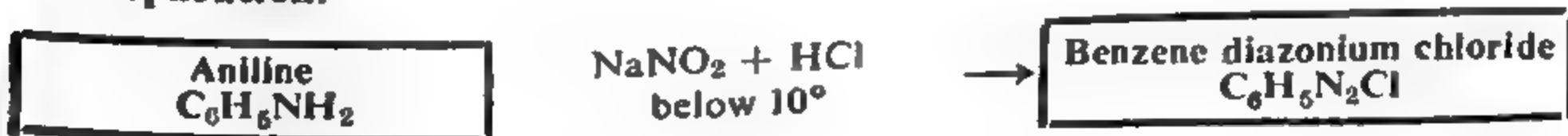
Probably there is a tautomerism between these two structures, *viz.*,



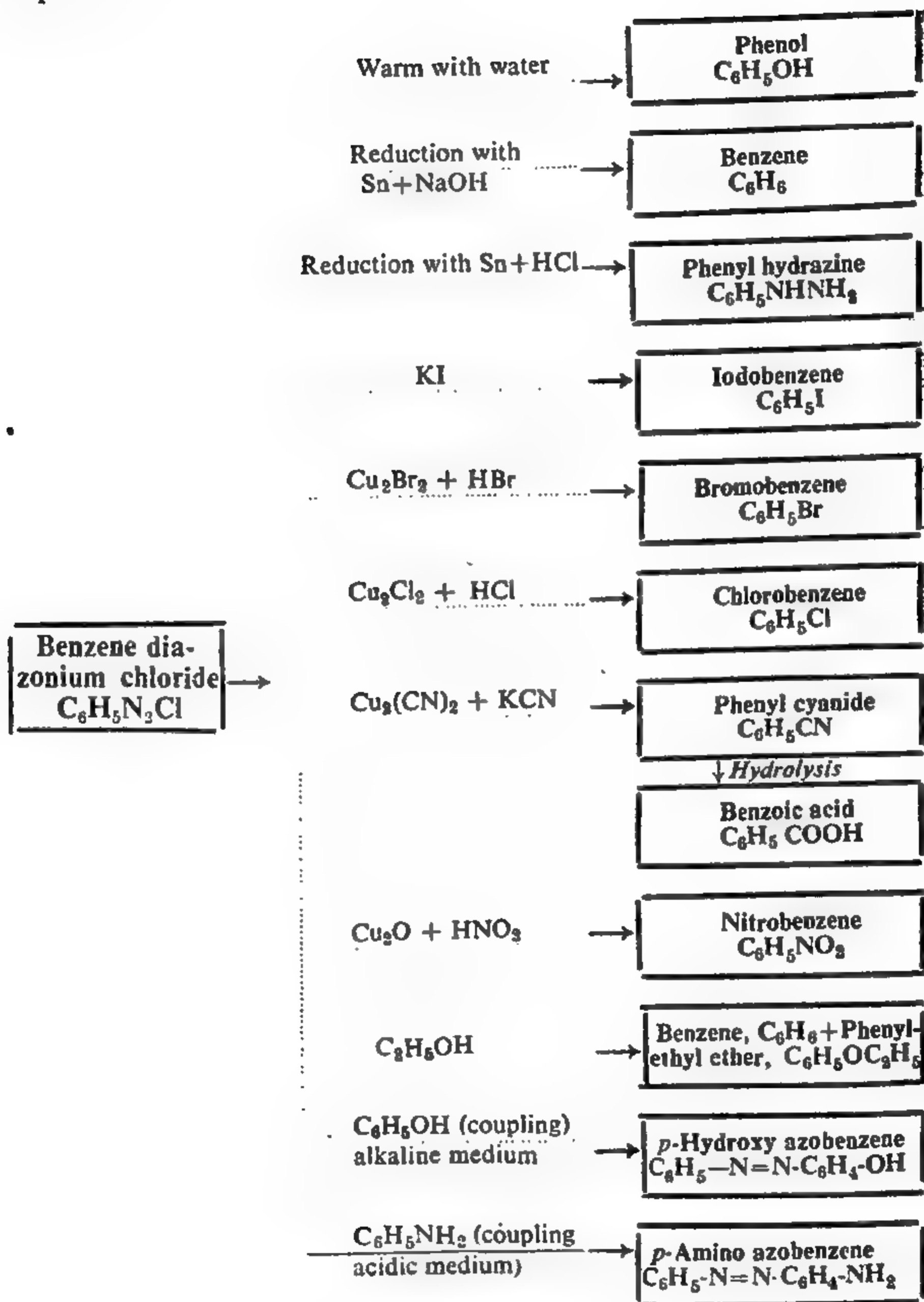
SUMMARY OF A TYPICAL MEMBER

PREPARATION AND PROPERTIES OF BENZENE DIAZONIUM CHLORIDE

Preparation.



Properties.



QUESTIONS

1. What are diazonium salts? What is their importance in aromatic chemistry?
2. Explain the term 'Diazotisation'. How will you diazotise aniline in laboratory? What are the essential conditions required?

3. How will you prepare benzene diazonium chloride in laboratory? How will it react with (a) boiling water (b) absolute alcohol (c) cuprous halide with the corresponding halogen acid (d) alkaline stannous chloride (e) phenol?
4. Write short notes on (a) the structure of the diazo salts (b) coupling (c) Sandmeyer's reaction (d) Gattermann's reaction.
5. How are diazo compounds prepared? Describe their reactions and importance in industry. *(Delhi Pre-medical 1954)*
6. How is diazo group introduced into benzene and what are characteristic reactions of this group? *(Panjab Inter 1960)*
7. Give the preparation and properties of benzene diazonium chloride. *(Panjab Inter 1959 S)*
8. Discuss in detail the use of benzene diazonium chloride in organic synthesis. *(Panjab Inter 1955)*
9. Give the preparation of benzene diazonium chloride. How does this compound react towards (i) aniline in hydrochloric acid (ii) stannous chloride in hydrochloric acid (iii) aqueous solution of potassium iodide (iv) cuprous cyanide solution in potassium cyanide? *(Panjab Inter 1950 S)*
10. Starting from benzene and with the help of diazo reaction, give the preparation of any four of the following:—(i) iodobenzene (ii) bromobenzene (iii) benzoic acid (iv) phenyl hydrazine (v) diazo amino benzene. *(Panjab Inter 1948)*

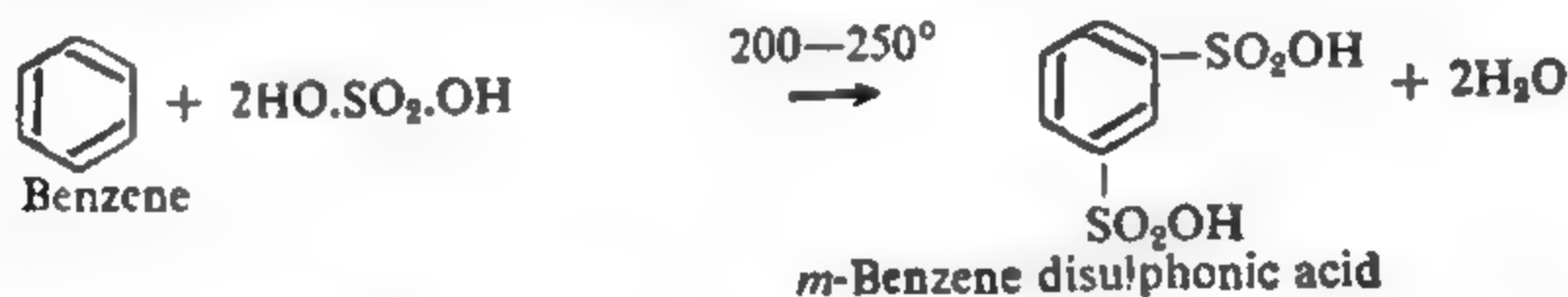
CHAPTER L

SULPHONIC ACIDS

Sulphonation. Benzene, when treated with concentrated sulphuric acid at 80° for 6—8 hours, gives *benzene sulphonic acid*, by the replacement of one hydrogen atom by sulphonic group.



This reaction is known as **sulphonation**. It is possible to introduce more than one sulphonic acid groups into the benzene ring; for instance, benzene when treated with an excess of fuming sulphuric acid at $200\text{--}250^{\circ}$ gives *m*-disulphonic acid.



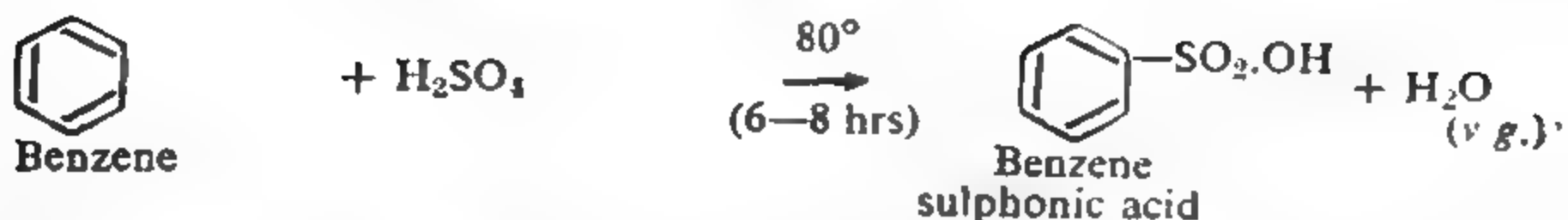
Salts of mercury, silver, vanadium and iodine catalyse the process of sulphonation. It has been observed that the presence of groups like methyl ($-\text{CH}_3$), hydroxyl ($-\text{OH}$) or primary amino ($-\text{NH}_2$), facilitates sulphonation, whereas groups like carboxyl ($-\text{COOH}$) or nitro ($-\text{NO}_2$) or sulphonic acid ($-\text{SO}_2\text{OH}$), retard further sulphonation.

Various sulphonating reagents such as concentrated sulphuric acid, fuming sulphuric acid, chlorosulphonic acid ($\text{Cl}\cdot\text{SO}_2\text{OH}$), sulphuryl chloride (SO_2Cl_2) in the presence of aluminium chloride, are available. The first named reagent is used if only one sulphonic acid group is to be introduced in the benzene ring. For introducing larger number of sulphonic acid groups fuming sulphuric acid (containing up to 70% of SO_3 dissolved in it) is very useful particularly in case of compounds containing $-\text{COOH}$ or $-\text{NO}_2$ or $-\text{SO}_2\text{OH}$ group (all meta-directing).

BENZENE SULPHONIC ACID, $\text{C}_6\text{H}_5\text{SO}_2\text{OH}$

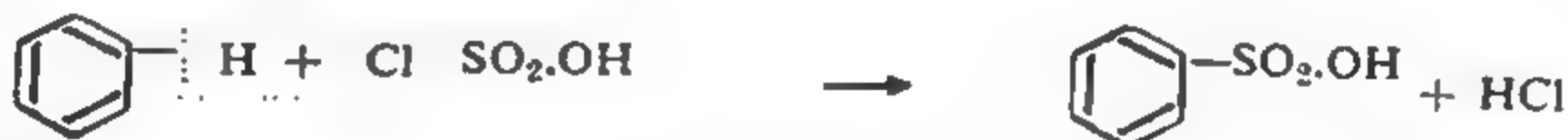
Preparation. Benzene sulphonic acid can be prepared :

(i) By heating benzene with concentrated sulphuric acid. At 80° benzene reacts with concentrated sulphuric acid according to the equation :



The water formed during the reaction dilutes the sulphuric acid and, therefore, the reaction slows down after sometime. In order to get a better yield, fuming sulphuric acid is used.

(ii) By the action of chloro-sulphonic acid on benzene. Chloro-sulphonic acid ($\text{Cl.SO}_2\text{SO}_2\text{OH}$) in carbon tetrachloride solution can also be used for sulphonating benzene.

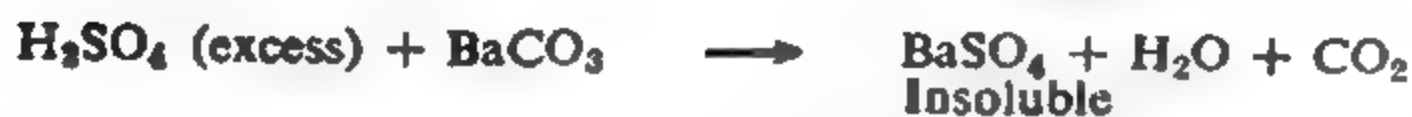


This method is advantageous in as much as no water is formed and hence the reaction does not slacken.

Laboratory Preparation. Benzene sulphonic acid is conveniently prepared in the laboratory by the following process :

Add benzene (1 part) to concentrated sulphuric acid (2 parts) contained in a round bottomed flask fitted with a reflux condenser, in small instalments at a time, with constant shaking and cooling if necessary. After the whole of benzene has been added, the reaction mixture is heated in an oil bath using an air condenser, until the benzene has completely dissolved in the acid. This shows that the sulphonation of benzene is complete.

The reaction mixture is poured in a large amount of cold water and the resulting solution is neutralised with powdered barium carbonate which combines with both the benzene sulphonic acid and excess of concentrated sulphuric acid forming barium benzene sulphonate (soluble) and barium sulphate (insoluble), respectively.



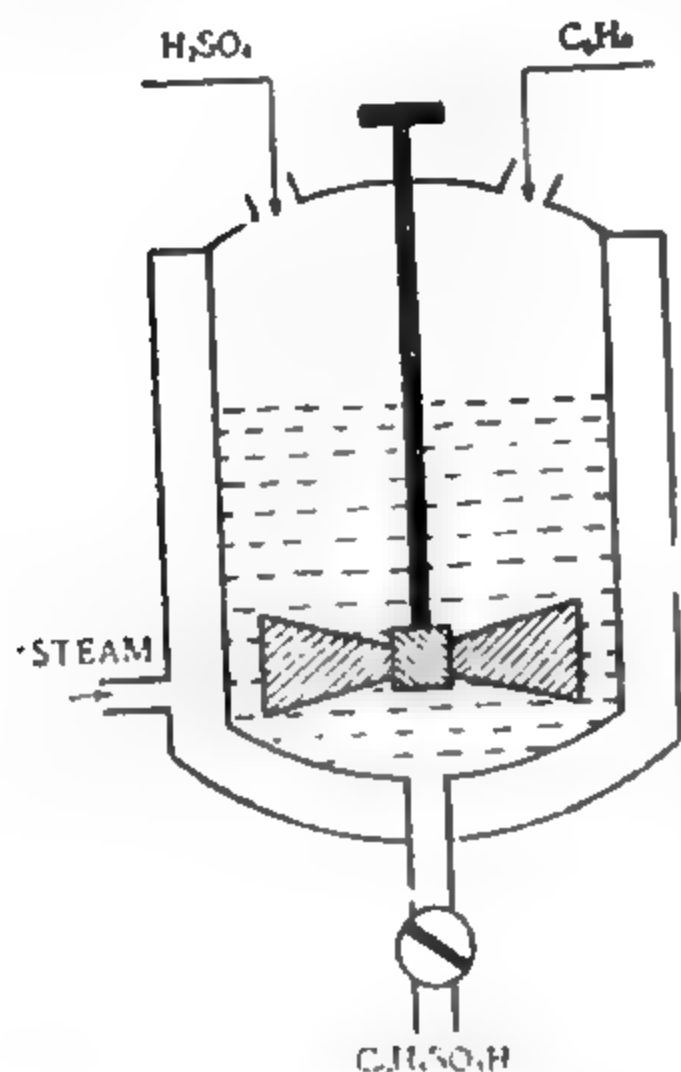
Thus, on filtration, the insoluble barium sulphate and excess of barium carbonate are retained on the filter paper, while barium benzene sulphonate, being soluble, comes down in the filtrate. The barium benzene sulphonate is treated with a calculated quantity of dilute sulphuric acid to regenerate the benzene sulphonic acid.



The insoluble barium sulphate is removed by filtration. The filtrate is concentrated and allowed to stand. Crystals of benzene sulphonic acid are obtained.

Alternatively, the reaction mixture, after sulphonation (i.e. containing benzene sulphonic acid and unreacted excess of sulphuric acid) is very gradually added to a saturated solution of sodium chloride contained in a beaker standing in ice-cold water when sodium benzene sulphonate separates as glistening plates (*salting out*) which are filtered off.

Manufacture. Benzene sulphonic acid, on a commercial scale, is also prepared by sulphonating benzene with concentrated sulphuric acid. The reaction is carried out in a steam jacketed enamelled or lead lined pan fitted with a mechanical stirrer. If need be, cold water can also be circulated through the outer jacket (Fig. 1). After the sulphonation is over, the charge is taken out from the bottom and treated as in the laboratory method.



Physical Properties. Benzene sulphonic acid is a colourless hygroscopic substance, which crystallises in plates having the composition $C_6H_5 \cdot SO_2 \cdot OH \cdot 1\frac{1}{2}H_2O$ (m.p. 44°). It is freely soluble in water and alcohol. Its aqueous solution is strongly acidic. Its lead and barium salts are soluble in water.

Chemical Properties. The chemical properties of benzene sulphonic acid can be studied under two headings.

(i) *Reactions of the sulphonic acid group.*

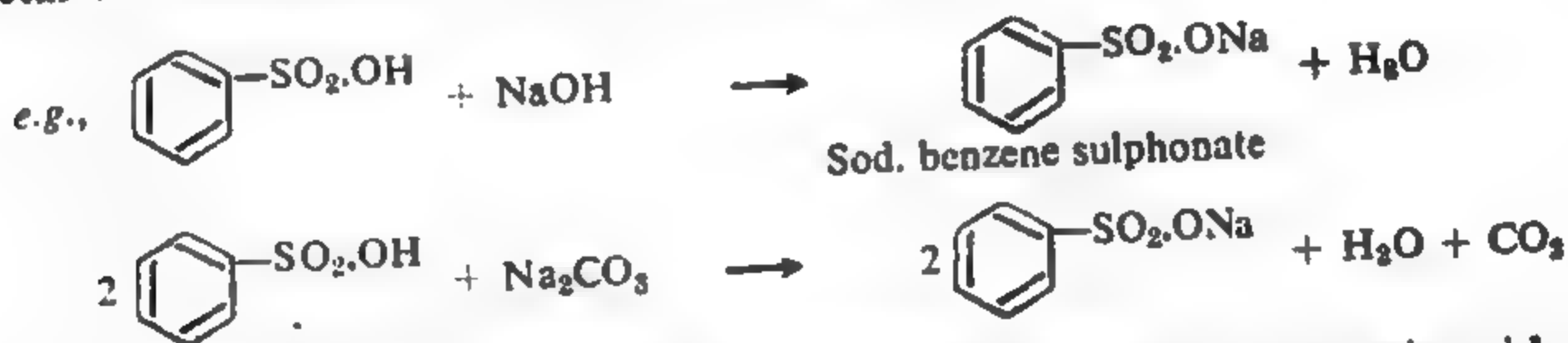
(ii) *Reactions of the nucleus.*

Fig. 1. Manufacture of benzene sulphonic acid

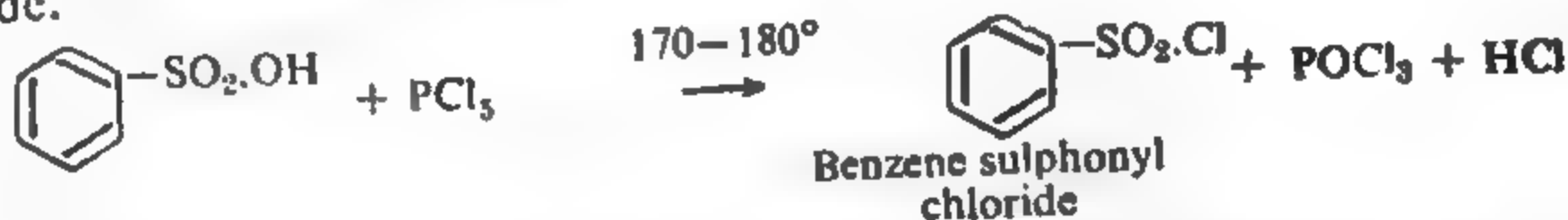
(i) Reactions of the Sulphonic Acid Group

1. Reaction with alkalis and carbonates.

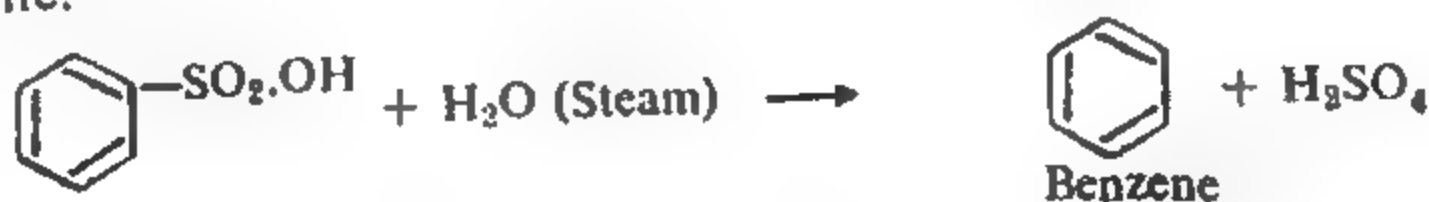
Benzene sulphonic acid being a strong acid reacts with alkalis and metal carbonates to form the corresponding salts.



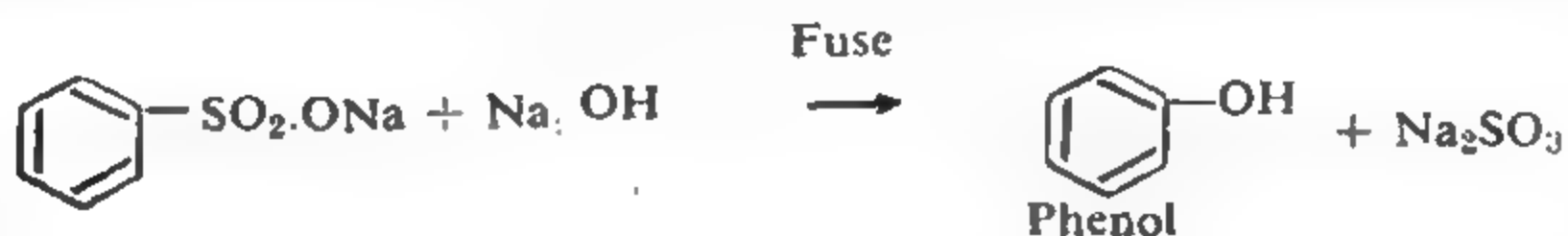
2. **Reaction with phosphorus pentachloride.** Benzene sulphonic acid reacts with phosphorus pentachloride to form the corresponding acid chloride.



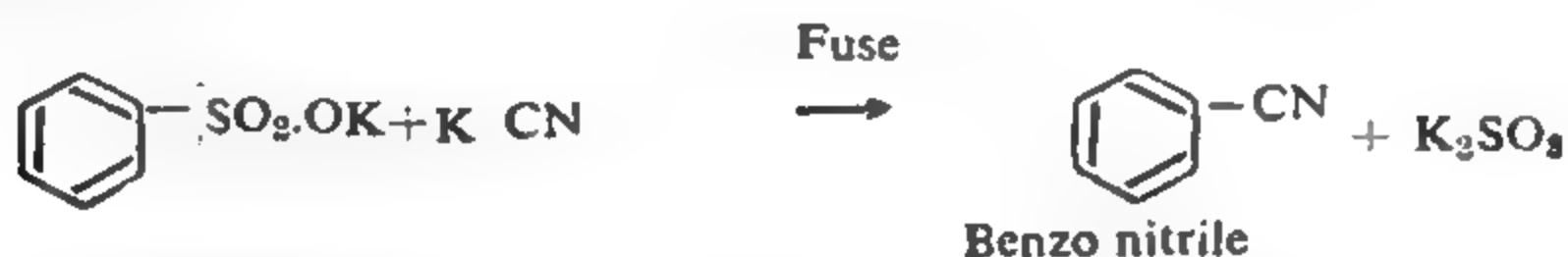
3. **Reaction with superheated steam (Hydrolysis).** Benzene sulphonic acid, when treated with superheated steam (or when heated with dilute hydrochloric acid) in a sealed tube (under pressure), gets hydrolysed to benzene.



4. **Reaction with alkalis at high temperature.** When sodium benzene sulphonate is fused with a large excess of sodium hydroxide in a nickel or silver dish, the sulphonic group is replaced by a hydroxyl group.

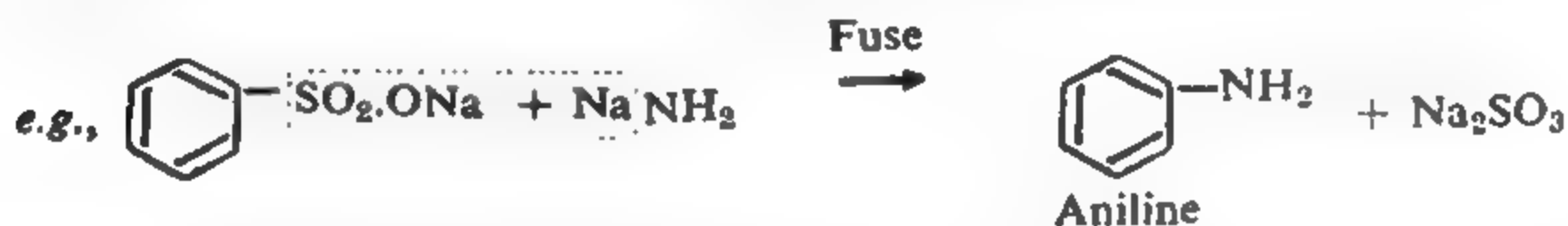


5. **Reaction with potassium cyanide.** The potassium salt on fusion with potassium cyanide yields the corresponding phenyl cyanide or benzo-nitrile.

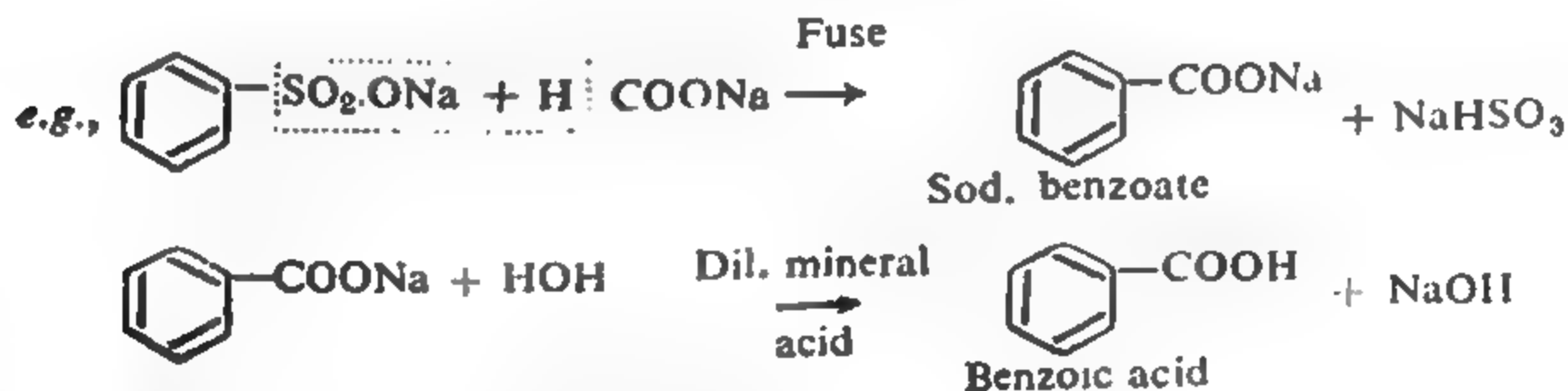


The phenyl cyanide can be hydrolysed or reduced to yield the corresponding acid or the primary amine.

6. **Reaction with sodamide.** The sodium salt of the acid on fusion with sodamide (Na.NH_2) yields the corresponding amino compound.

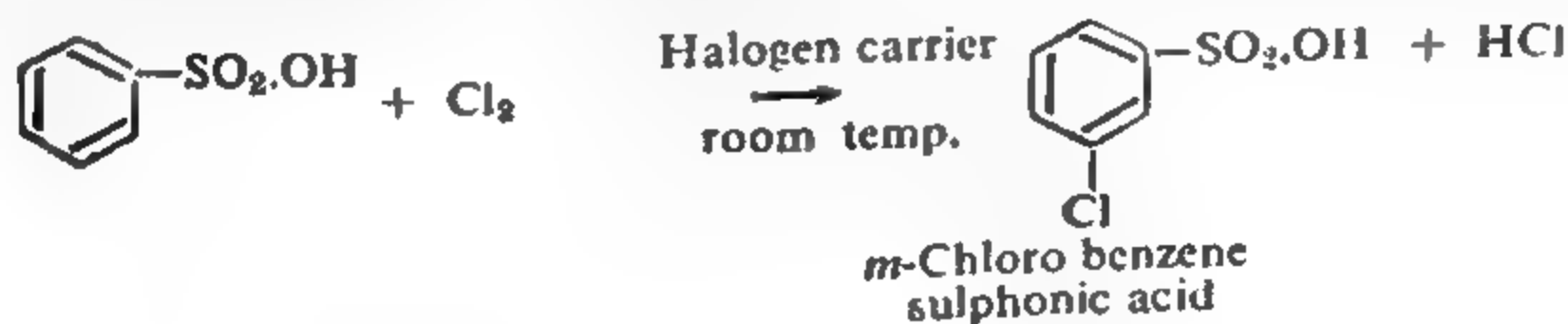


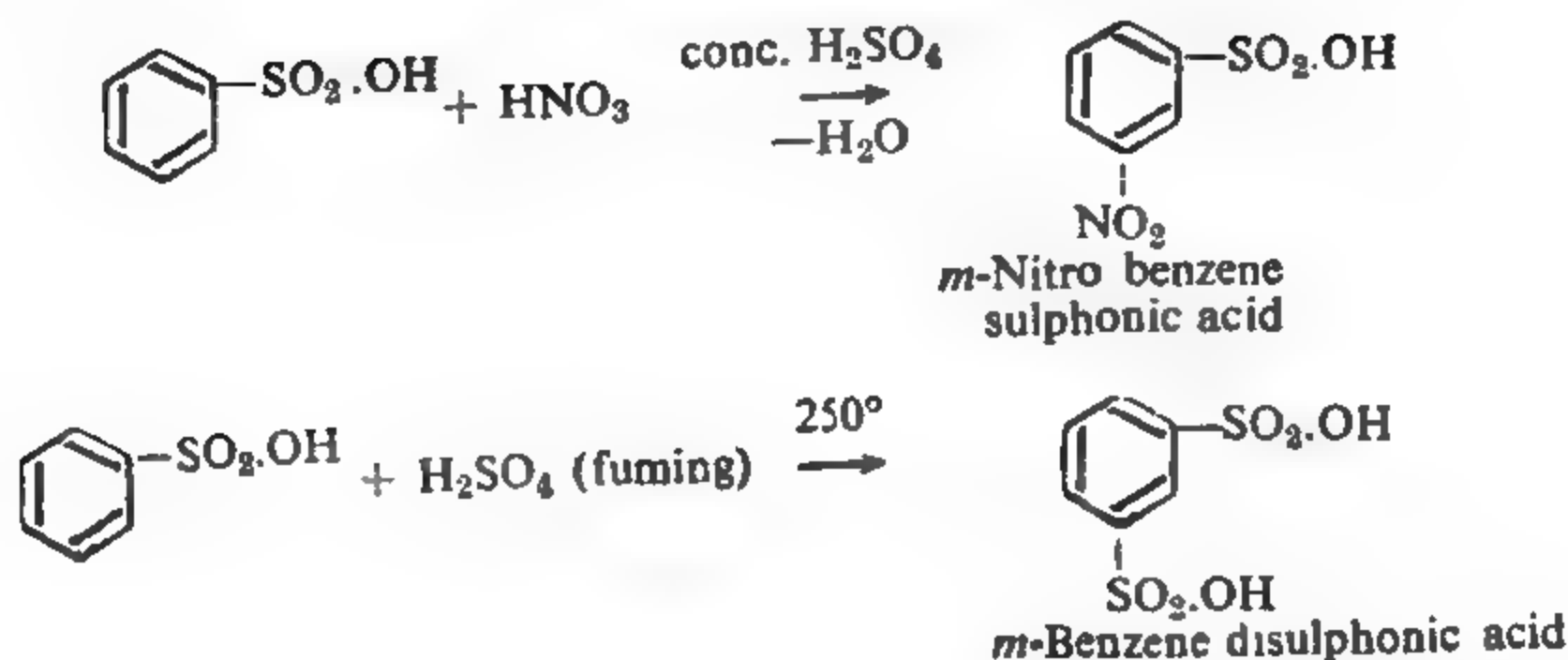
7. **Reaction with sodium formate.** The sodium salt of benzene sulphonc acid, when fused with sodium formate, yields sodium benzoate which on hydrolysis forms benzoic acid.



(ii) Reactions of the Benzene Nucleus

Benzene sulphonc acid undergoes halogenation, nitration and sulphonation to form the corresponding meta-derivative in each case.

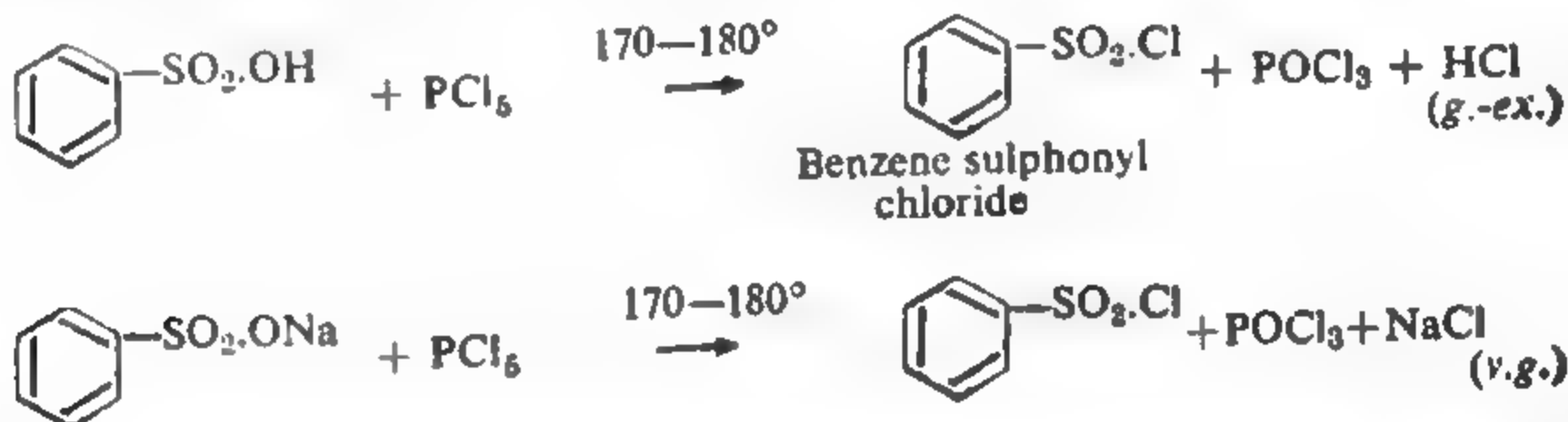




Uses. Benzene sulphonic acid is an important starting material for the preparation of quite a large number of benzene derivatives. It is an intermediate in the preparation of dyes and drugs. Sodium salts of alkyl derivatives of benzene sulphonic acid (e.g., $\text{R.C}_6\text{H}_4\text{SO}_2\text{ONa}$) are used as detergents.

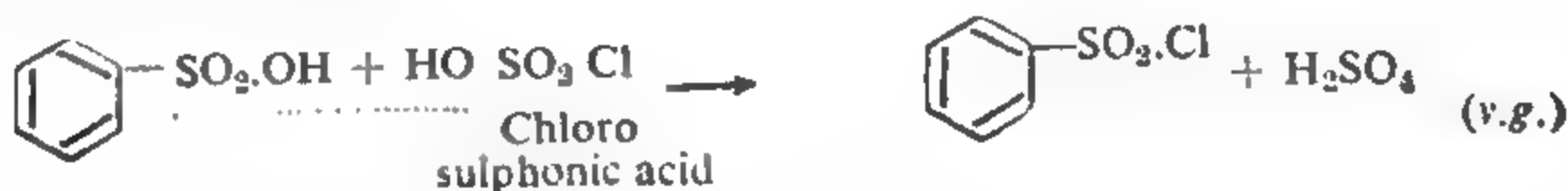
Benzene sulphonyl chloride, Hinsberg's reagent, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$

Preparation. Benzene sulphonyl chloride is prepared by heating benzene sulphonic acid or its sodium salt with phosphorus pentachloride at $160-180^\circ$ for some hours.



The reaction mixture is cooled and poured into water. Being immiscible, benzene sulphonyl chloride forms a separate layer. It is recovered by means of a separating funnel and purified by distillation under reduced pressure.

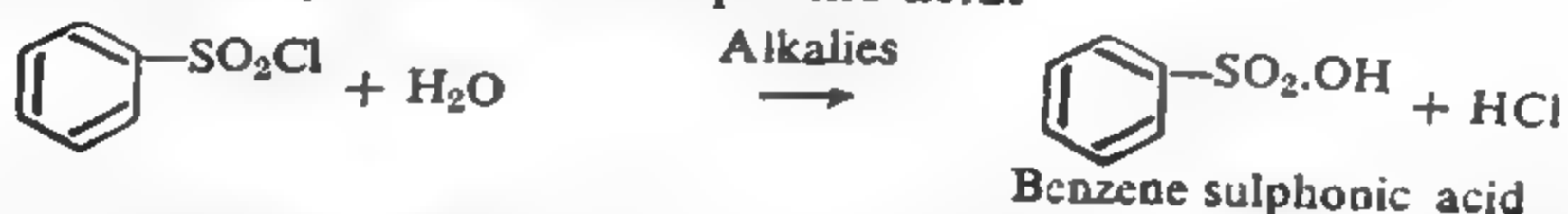
(2) It can also be prepared by treating benzene with an excess of chlorosulphonic acid.



Physical Properties. Benzene sulphonyl chloride is a colourless oily liquid (b.p. 251°). It is insoluble in water but soluble in ether. It has a characteristic unpleasant odour and has a lachrymatory effect (i.e. causing watering of eyes, nose, etc).

Chemical Properties. It gives the following reactions :

(1) **Hydrolysis.** It is slowly hydrolysed with water but more readily with alkalis, to give benzene sulphonic acid.



(2) **Ester formation.** With ethyl alcohol, it reacts to form ethyl sulphonate.



(3) **Amide formation.** When shaken with concentrated ammonia, it gives a precipitate of benzene sulphonamide.

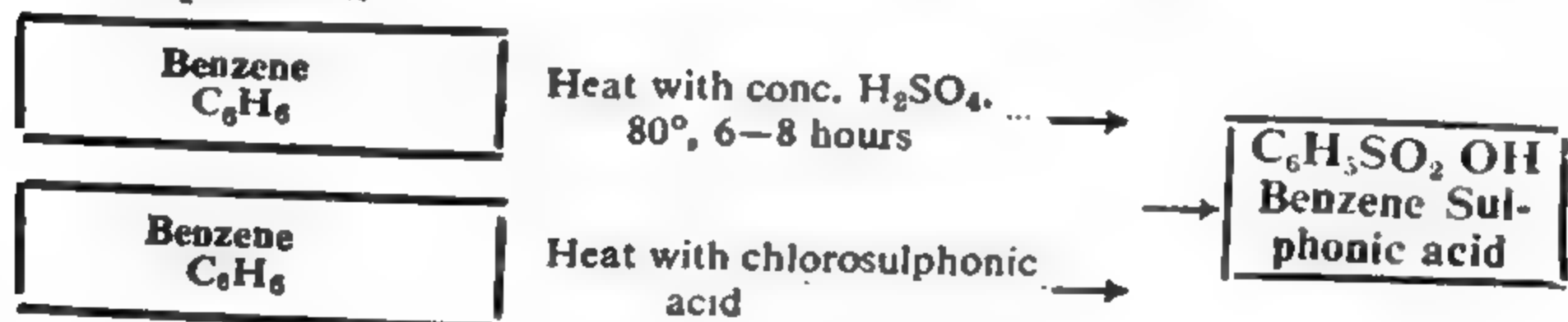


(4) **Reaction with primary and secondary amines.** It reacts with primary and secondary amines to form substituted amides. Since it does not react with tertiary amine, it is used for the separation of primary, secondary and tertiary amines under the name of Hinsberg's reagent.

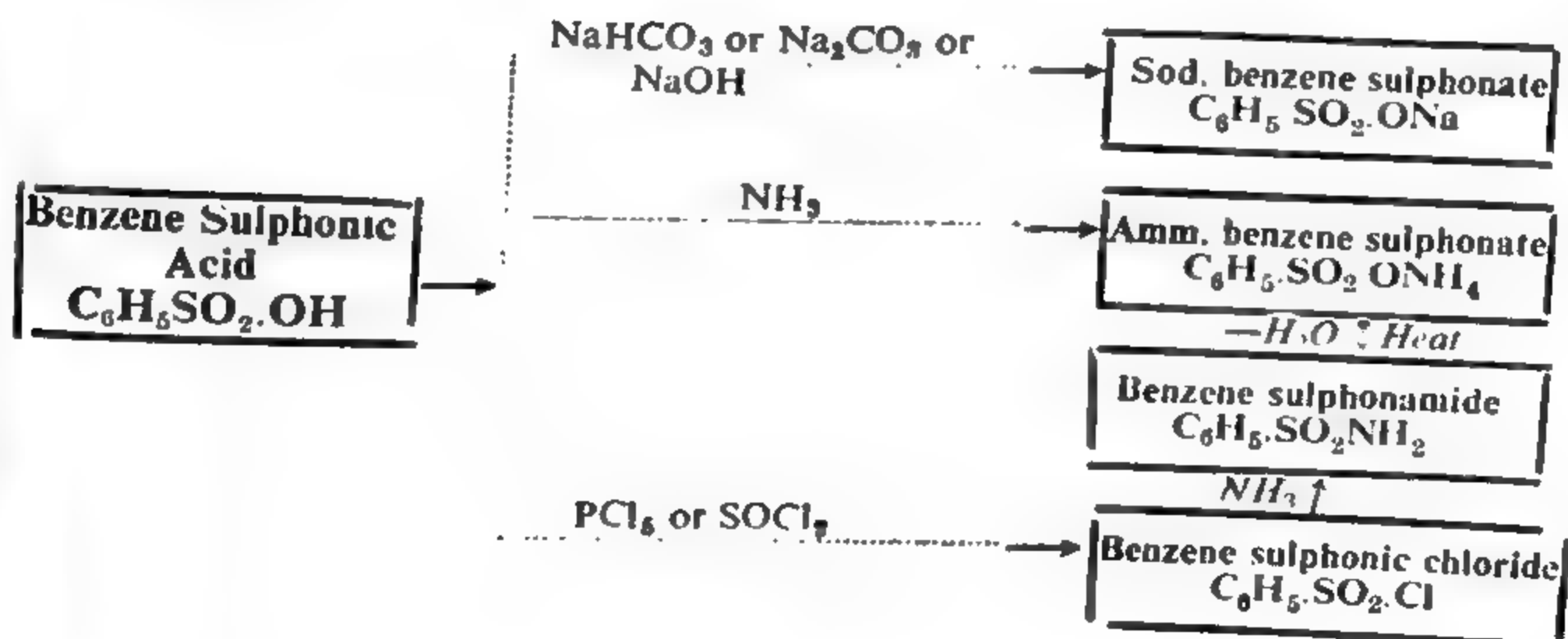
SUMMARY OF A TYPICAL MEMBER

PREPARATION AND PROPERTIES OF BENZENE SULPHONIC ACID

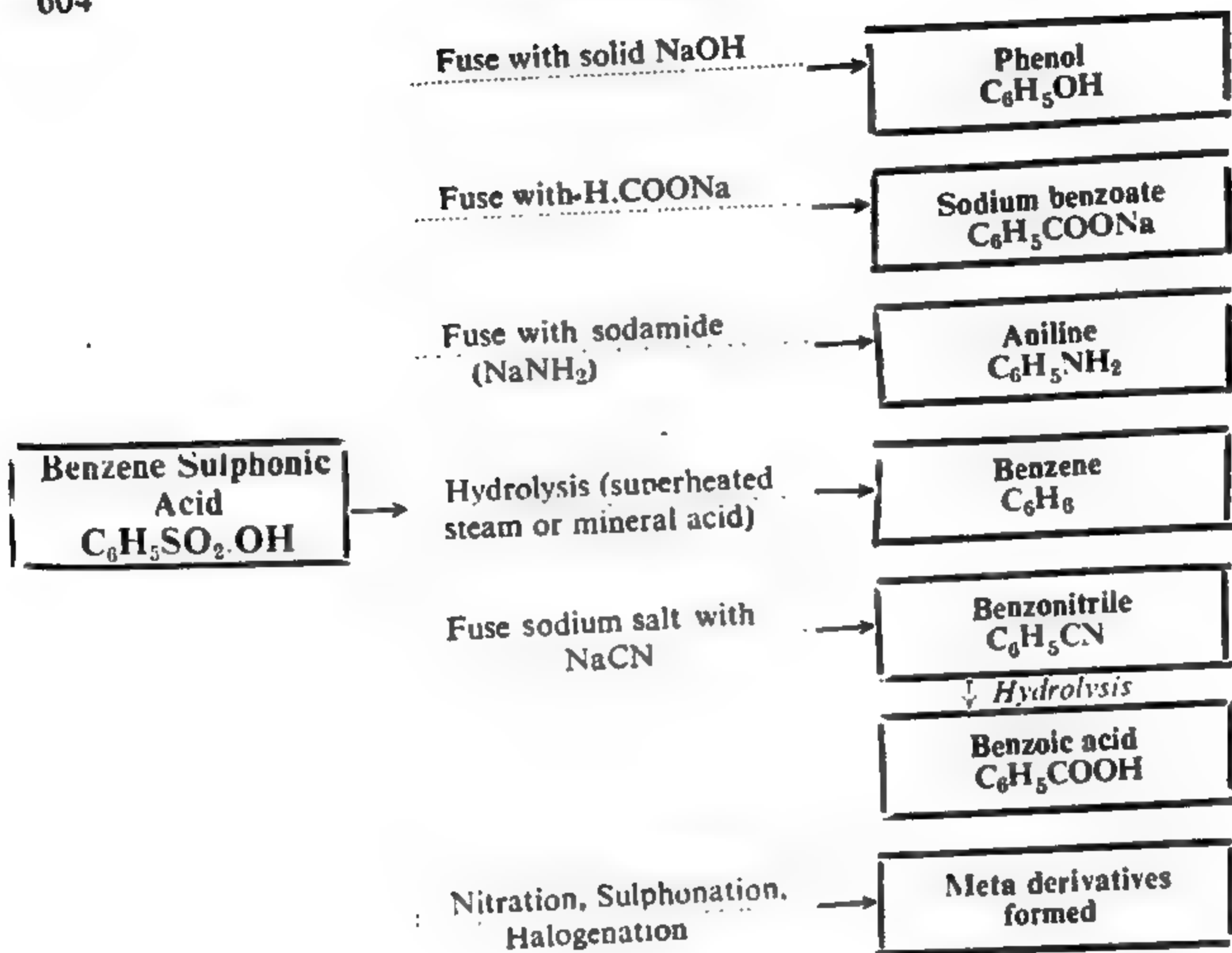
Preparation.



Properties.



QUESTIONS



QUESTIONS

1. What do you understand by the term sulphonation? How will you prepare a sample of benzene sulphonic acid in laboratory? What are its uses?
2. Describe the preparation, properties and uses of Hinsberg's reagent.
3. Give the laboratory preparation, four properties and two outstanding uses of benzene sulphonic acid. *(Panjab Inter 1955)*
4. How is benzene sulphonic acid prepared? Show by reactions how it can be converted into:
(a) benzene (b) phenol (c) benzoic acid (d) aniline and (e) *m*-benzene disulphonic acid. *(Panjab Inter 1957)*
5. Give in detail the preparation of benzene sulphonic acid in the laboratory.
How can you get from the acid (a) phenol (b) benzoic acid (c) benzene and (d) benzene sulphonyl chloride? *(Panjab Inter 1962)*

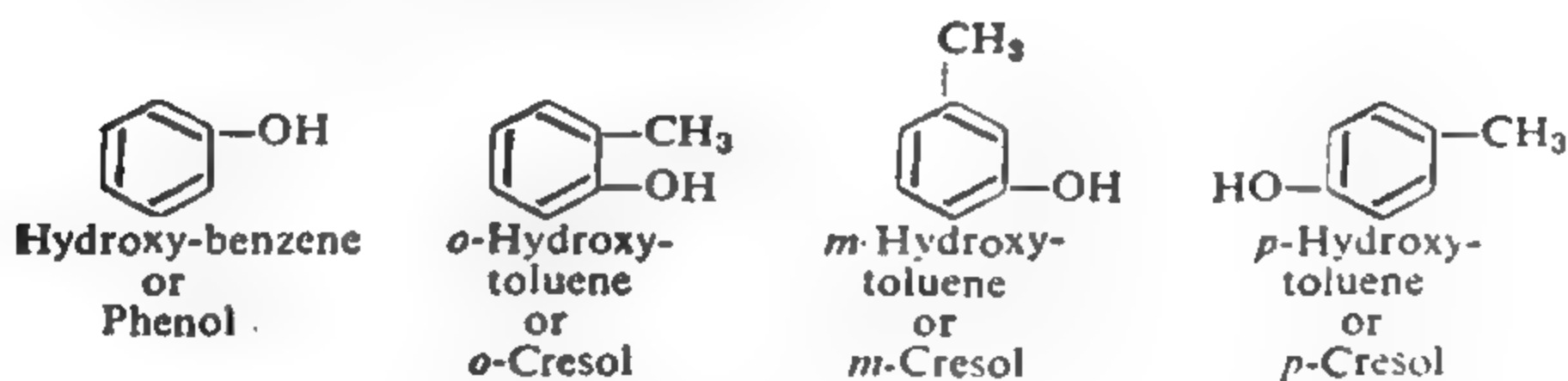
CHAPTER LI

PHENOLS AND AROMATIC ALCOHOLS

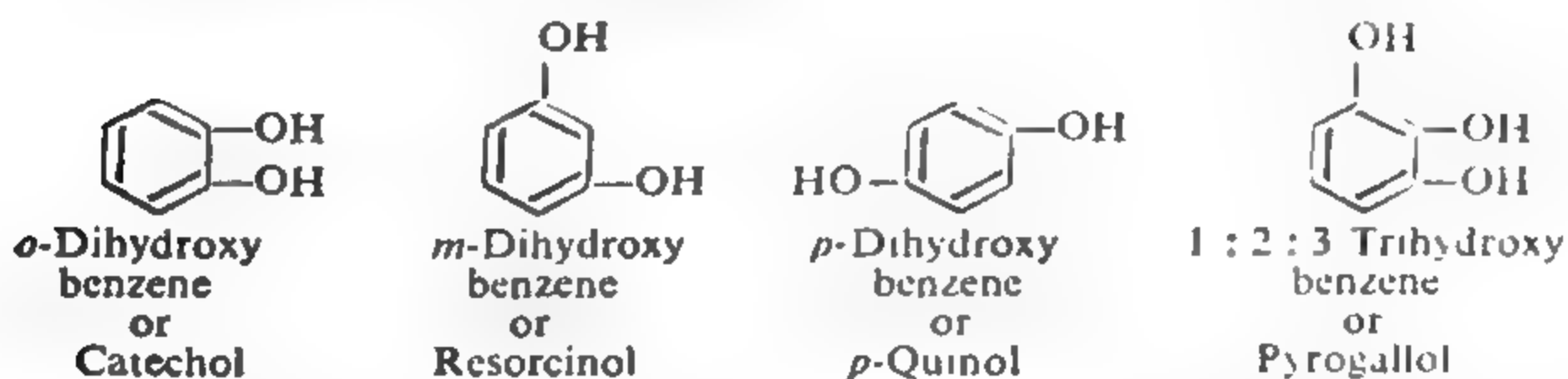
There are two types of aromatic hydroxy compounds : (i) *Phenols* and (ii) *Aromatic alcohols*.

(a) **Phenols.** The compounds in which the hydroxyl group is directly attached to the benzene nucleus are called **phenols**.

Examples of such compounds are :



Di- and tri- hydric phenols are also known. For example,



(b) **Aromatic Alcohols.** The compounds in which the hydroxyl group is attached to the side chain are called **aromatic alcohols**. Examples of such compounds are :



Phenol and aromatic alcohols differ considerably from each other in their physical and chemical properties as will be shown presently.

Phenols are far more important from the industrial point of view. They are the starting materials for the manufacture of disinfectants, plastics, explosives, etc.

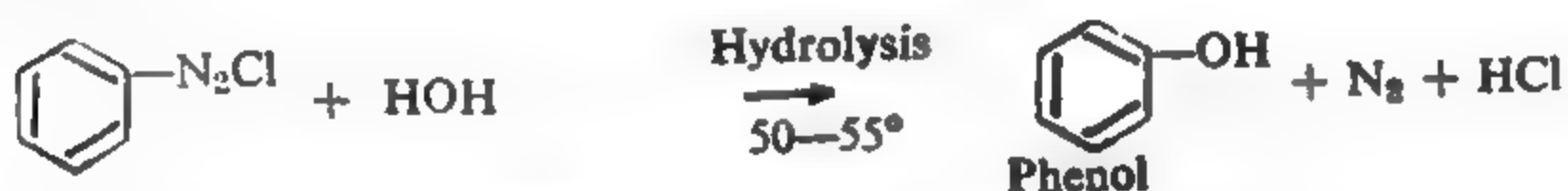
PHENOL, HYDROXY-BENZENE, C_6H_5OH

(*Carbolic Acid*)

Phenol is a representative member of the phenol series. It was discovered in coal tar in 1833 by Runge who named it **carbolic acid** (*carbo* = coal, *oleum* = oil). It is the principal constituent of the 'middle oil' fraction of the coal tar distillation.

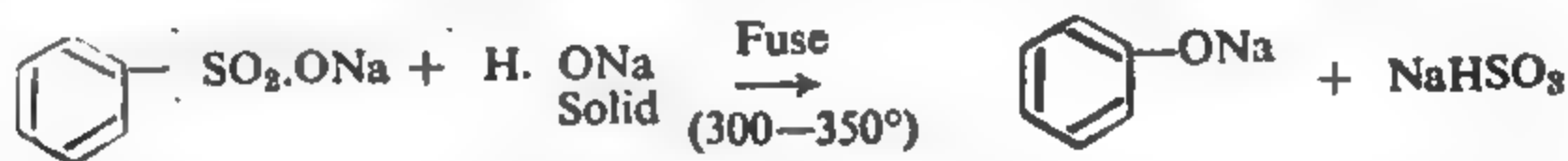
Preparation. Phenol may be prepared by any of the methods discussed below :

1. **By the hydrolysis of benzene diazonium chloride.** If an aqueous solution of benzene diazonium chloride is gently warmed to $50-55^\circ$, nitrogen is evolved and a dark coloured solution containing phenol is obtained.

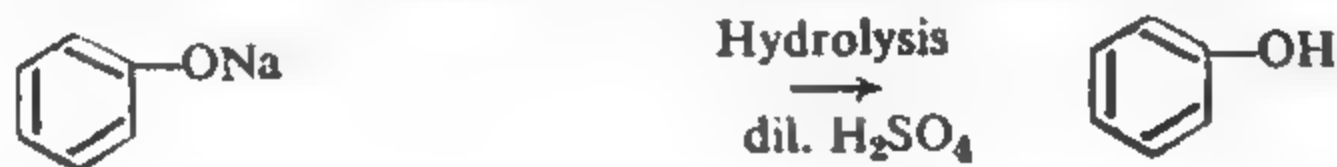


The dark-coloured solution is steam distilled and the distillate is extracted with ether. The ethereal solution containing phenol is dried with anhydrous potassium carbonate and fractionally distilled using an air condenser.

2. **By fusing sodium benzene sulphonate with solid sodium hydroxide.** If sodium benzene sulphonate is mixed with a large excess of sodium hydroxide and a little water in a nickel or an iron dish and the reaction mixture heated gradually to about $300-350^\circ$, sodium phenate is formed.



The resulting mass is dissolved in water and acidified with dilute sulphuric acid to liberate phenol which is recovered as in (1).



This was the first method employed for the commercial preparation of phenol.

*Benzene diazonium bisulphate is a more suitable reagent, as a part of $C_6H_5N_2Cl$ decomposes to yield chlorobenzene, due to the side reaction

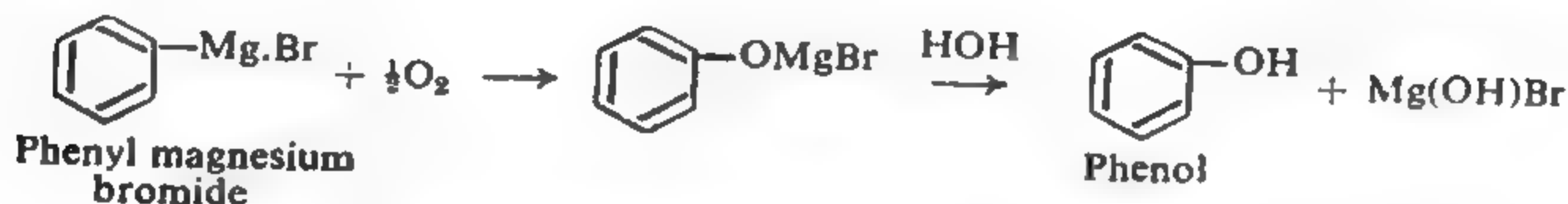


Thus, C_6H_5Cl will be present as an impurity in the phenol obtained from benzene diazonium chloride.

3. By the decarboxylation of the corresponding hydroxy acid by heating with soda lime. In this method, sodium salicylate is mixed with soda lime and the mixture distilled.



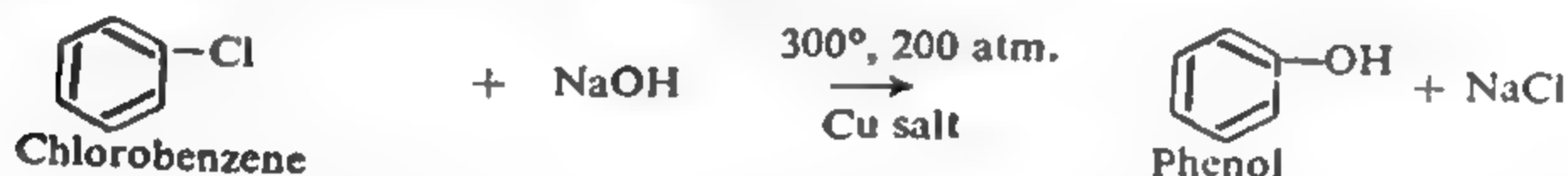
4. By the hydrolysis of the oxygen compound of the corresponding Grignard reagent.



Manufacture. Phenol is manufactured by the following methods :

1. **From coal tar.** Phenol is recovered from the middle oil fraction of coal tar distillation, as described earlier.

2. **From chlorobenzene (Dow's process).** In this method chlorobenzene is heated with a 10% solution of sodium hydroxide or sodium carbonate at about 300° and under 200 atmospheres pressure in the presence of a copper salt (catalyst).

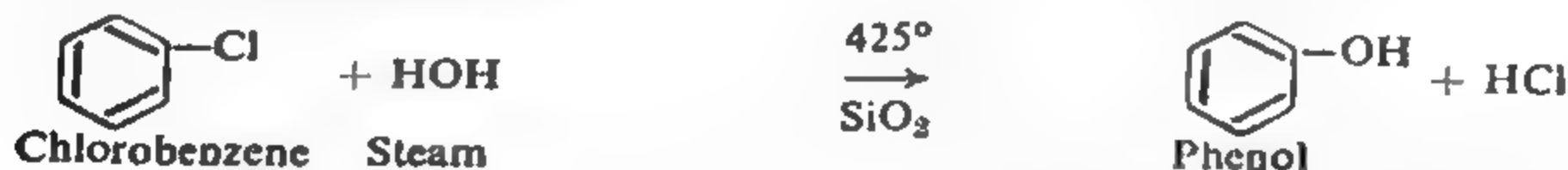


Phenol is recovered from the resulting solution by steam distillation.

3. **From benzene. (Rasching's process).** A mixture of benzene vapour, hydrogen chloride and air (or oxygen) is passed over copper chloride heated to 230°.



The chlorobenzene formed is heated with steam at 425° in the presence of silica catalyst.



The hydrogen chloride obtained in the second step is used over again. Thus, in effect, this process consists simply in the oxidation of benzene with oxygen and is, therefore, very economical.

This method has been extensively used in the United States and Germany since 1940.

Physical Properties. Phenol is a colourless, crystalline solid (m.p. 41°) hygroscopic in character. It turns pink on exposure to air and light. It possesses a strong phenolic odour. It is partially miscible with water, but dissolves readily in hot water, alcohol and ether. It is volatile in steam. It is very corrosive, forms blisters when brought into contact with skin and is poisonous.

Chemical Properties. The chemical reactions of phenol may be studied under the following heads :

(i) *Reactions of the hydroxyl group* (ii) *Reactions of the benzene nucleus* (iii) *Special reactions.*

(1) Reactions of the Hydroxyl Group.

1. **Acidic character.** Phenol is feebly acidic in character. In aqueous solution, it dissociates slightly as :



Thus, its aqueous solution turns blue litmus red.

It forms salts with strong alkalis like sodium hydroxide and potassium hydroxide.



But it is too weak to decompose a carbonate (difference from an acid).

2. **Reaction with metallic sodium.** Phenol reacts with sodium metal to form sodium phenate.



3. **Reduction with zinc dust.** Phenol is reduced to benzene when its vapour are passed over heated zinc dust.

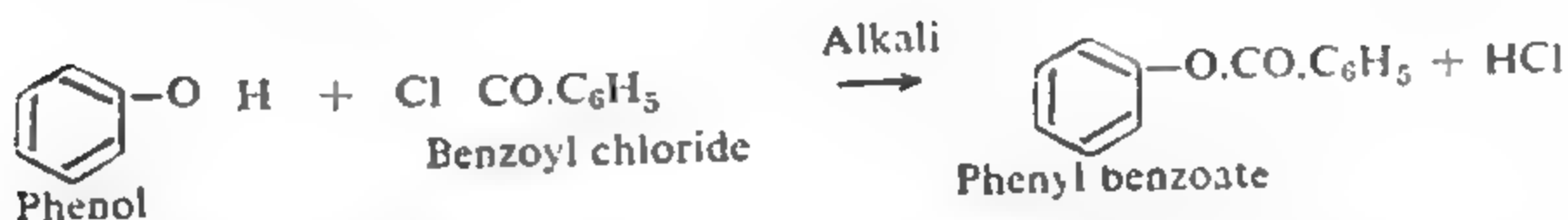
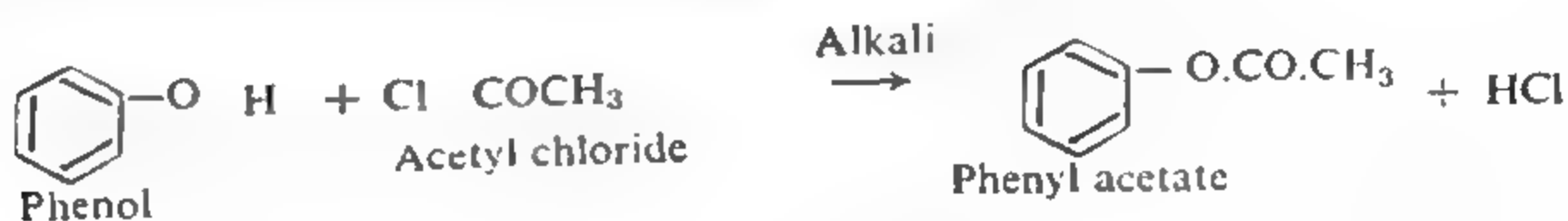


4. **Reaction with phosphorus pentachloride.** Phenol reacts with phosphorus pentachloride to form chlorobenzene.



5. **Reaction with acid chlorides.** Phenol reacts with acetyl chloride, acetic anhydride or benzoyl chloride in the presence of pyridine or dilute

sodium hydroxide to form the corresponding ester. The hydrogen atom of the—OH group is replaced by the corresponding acyl group.



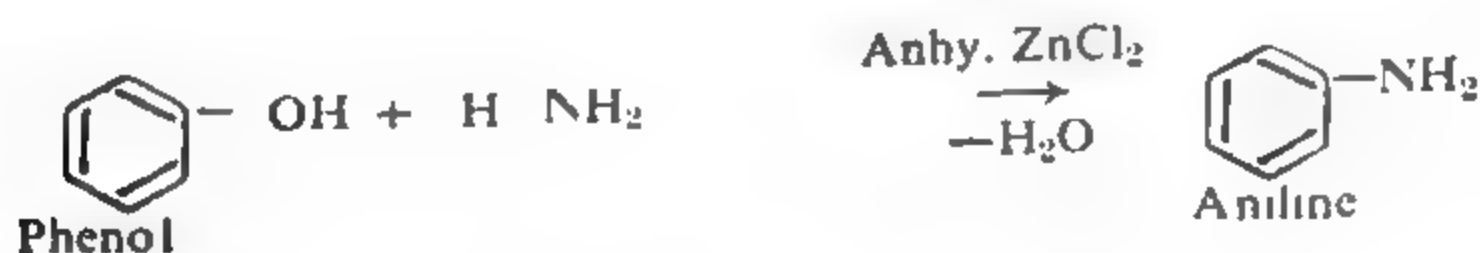
The reaction with benzoyl chloride is known as Schotten-Baumann reaction.

6. **Reaction with alkyl halides.** Sodium salt of phenol reacts with alkyl halides to form the corresponding mixed ethers.



The above reaction may also be carried out by passing vapours of phenol and alcohol over heated thoria or alumina (*cf.* preparation of ethers).

7. **Reaction with ammonia.** Phenol reacts with ammonia, in the presence of anhydrous zinc chloride, to form aniline.

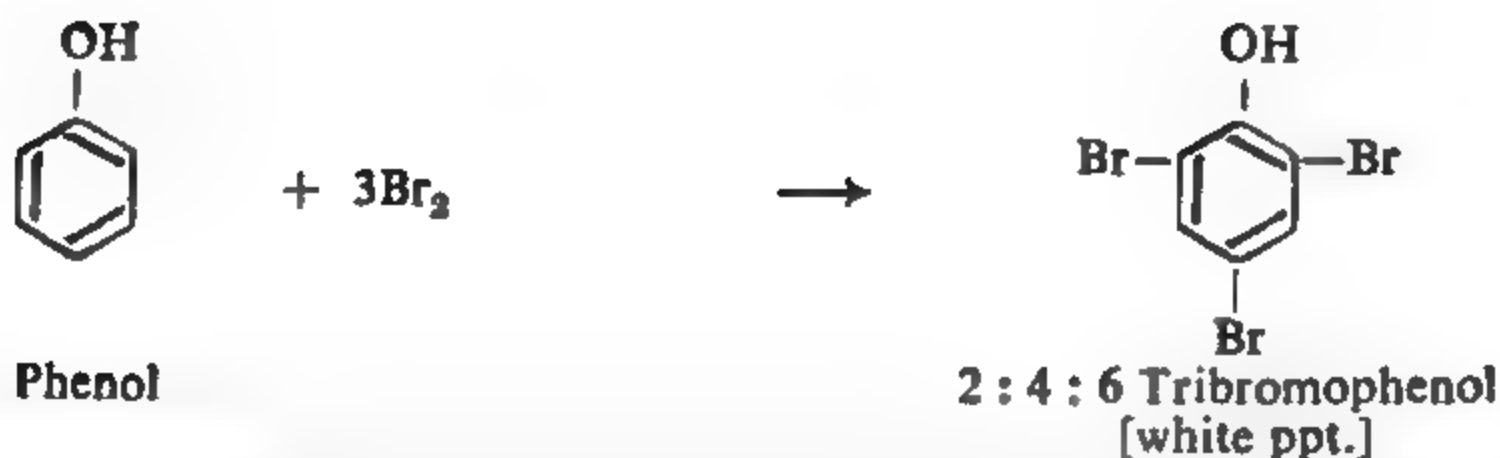


8. **Reaction with ferric chloride.** Phenol reacts with neutral ferric chloride to give a blue or violet coloration. This reaction is characteristic of all compounds containing a phenolic group.

(ii) Reactions of the Benzene Nucleus

Phenol undergoes the usual reactions of the benzene nucleus. It can be nitrated, halogenated, and sulphonated. The benzene ring can also be hydrogenated.

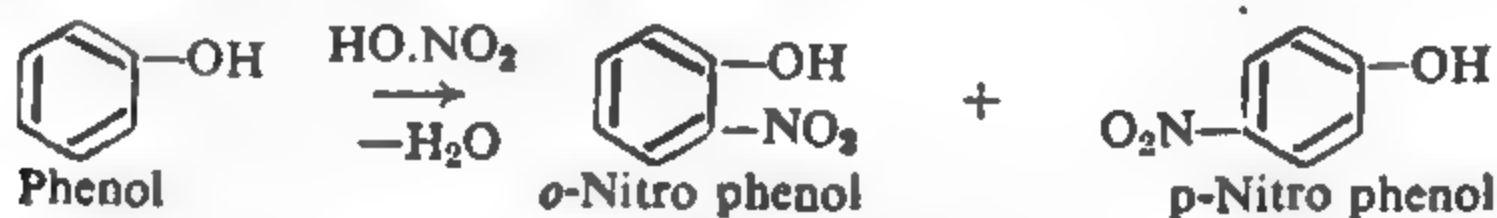
1. **Halogenation.** Phenol can be chlorinated or brominated more readily than benzene. The —Cl or —Br group can be introduced into the nucleus even on treatment with chlorine or bromine water at room temperature. Under these conditions, the di- and tri-halogenated products are immediately formed.



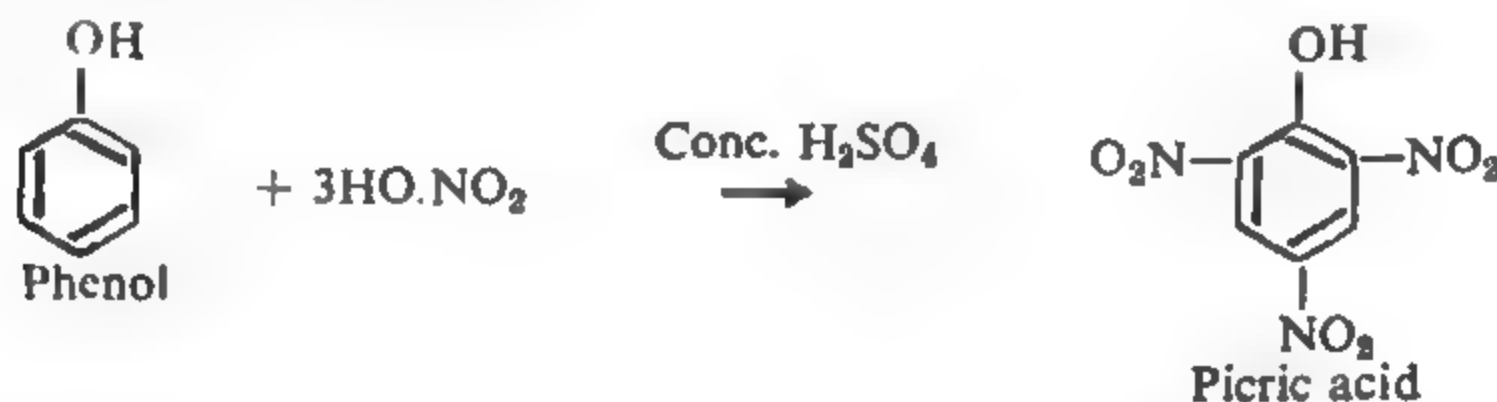
This reaction is used for qualitative and quantitative estimation of phenol.

2. Nitration. Phenol undergoes nitration more easily than benzene.

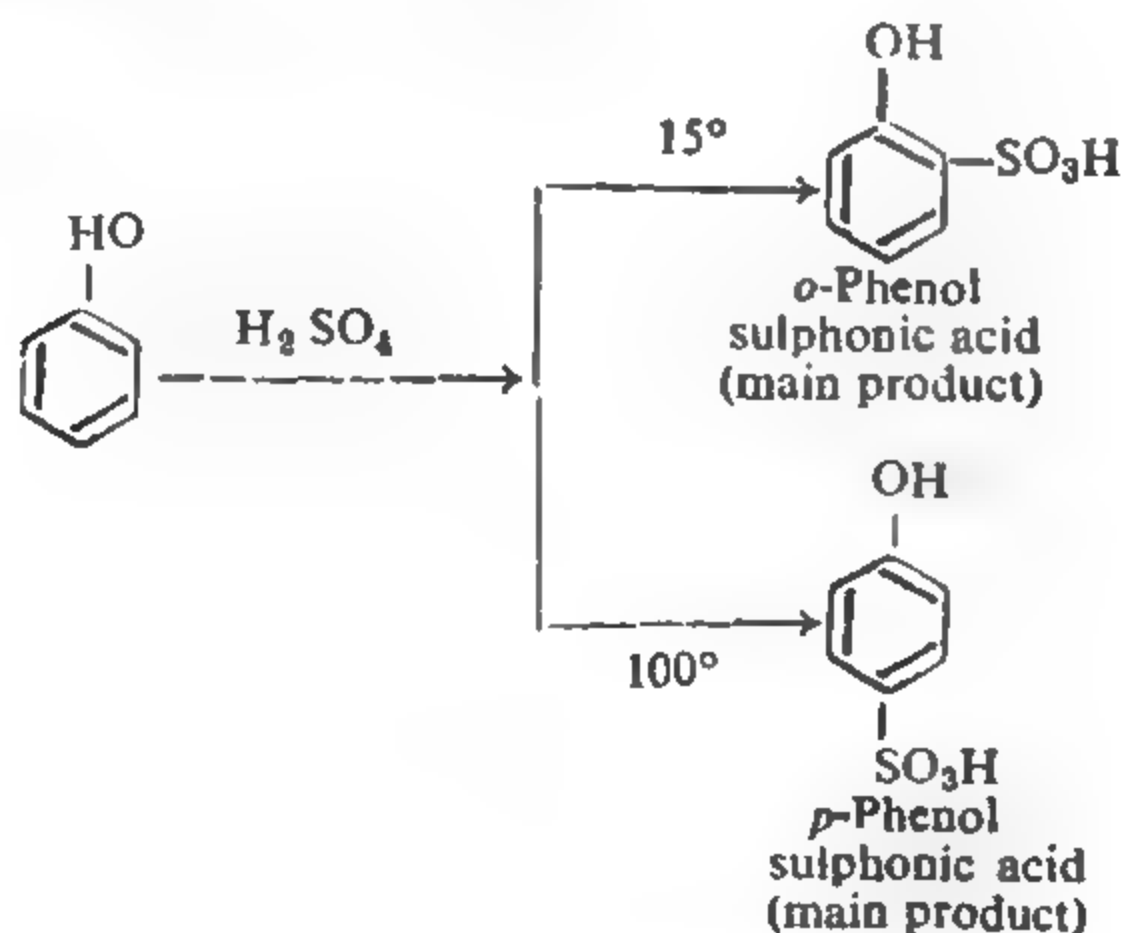
(a) With dilute nitric acid (1 part diluted with 3 parts of water), phenol forms *o*- and *p*-nitro phenols.



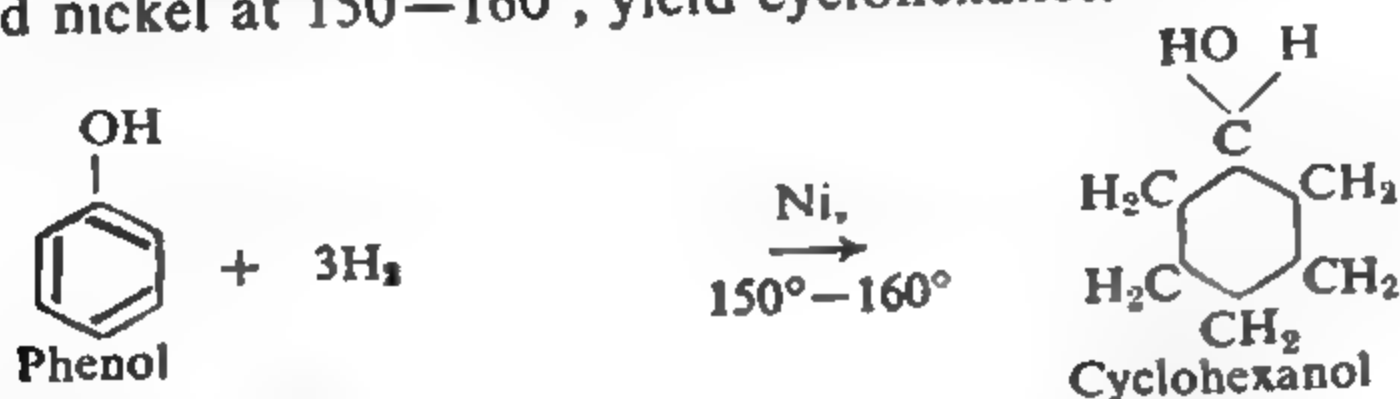
(b) With concentrated nitric acid, in the presence of conc. sulphuric acid, it reacts to yield picric acid (2 : 4 : 6 trinitro phenol), a brilliant yellow coloured compound.



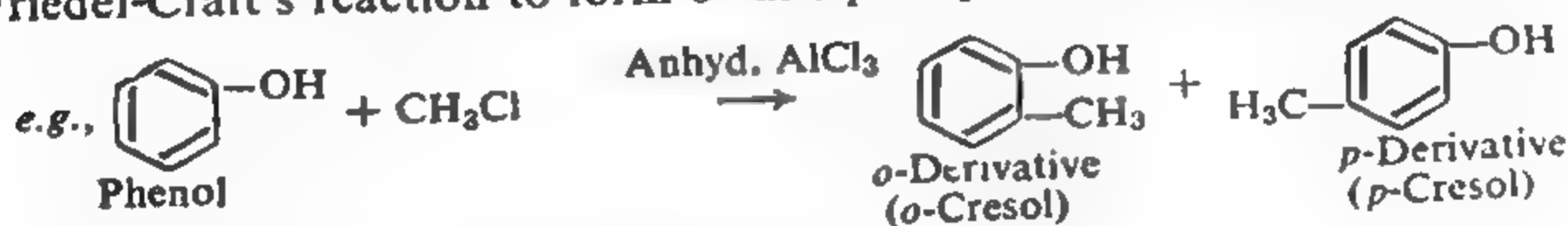
3. Sulphonation. Sulphonation of phenol is very easy. Simple dissolving phenol in concentrated sulphuric acid at room temperature yields a mixture of *o*- and *p*-sulphonic acids, the relative composition depending upon the temperature of the reaction. Low temperatures favour ortho-sulphonation whereas high temperatures favour the formation of para isomers.



4. **Hydrogenation.** Phenol vapours and hydrogen, when passed over heated nickel at $150-160^\circ$, yield cyclohexanol.



5. **Alkylation.** (Friedel and Craft's reaction). Phenol undergoes Friedel-Craft's reaction to form *o*- and *p*-alkyl-substituted derivatives.



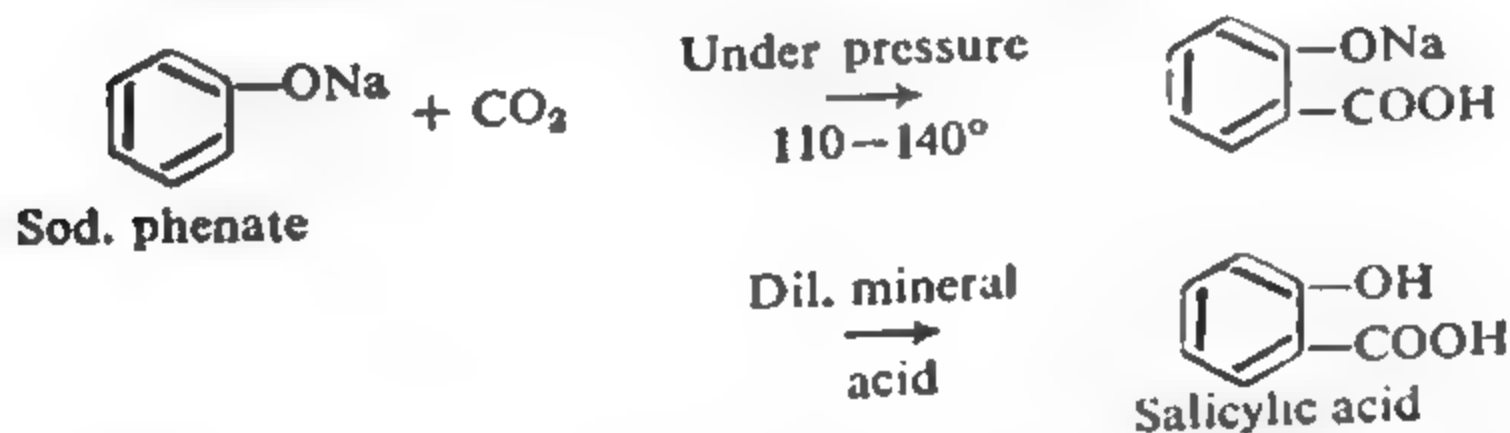
In this reaction para derivative is the main product.

(iii) Special Reactions.

1. **Liebermann's Nitroso Reaction.** A small amount of phenol is heated gently with a few crystals of sodium nitrite for a short while and a few drops of concentrated sulphuric acid are added. A deep green or deep blue colour develops. If this reaction mixture is poured in a beaker of water, the colour becomes red which again turns blue or green on the addition of an excess of sodium hydroxide.

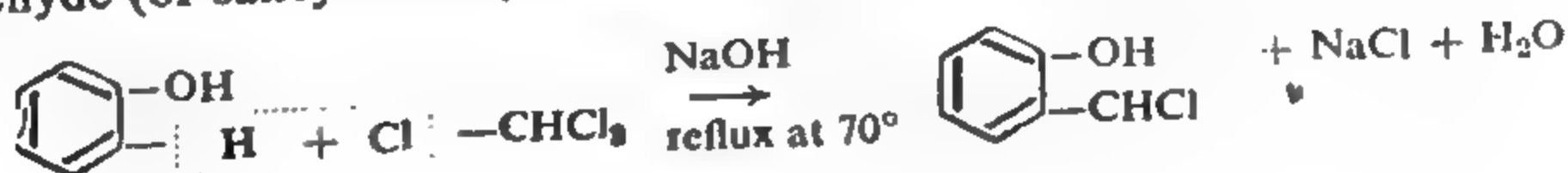
2. **Kolbe's Reaction.** Sodium salt of phenol reacts with carbon dioxide under pressure (1.5 atmospheres) at $120-140^\circ$ to give *o*-hydroxy benzoic acid, *i.e.*, salicylic acid.

The reaction is supposed to take place as under :

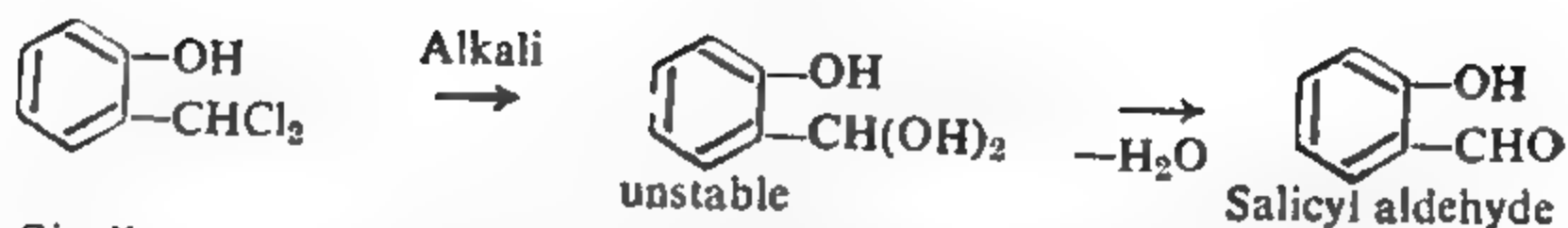


Some *p*-compound is also produced simultaneously, but the main product is the ortho-compound.

3. **Reimer-Tiemann's Reaction.** Phenol reacts with chloroform (or carbon tetrachloride) in the presence of sodium hydroxide to yield salicylaldehyde (or salicylic acid).



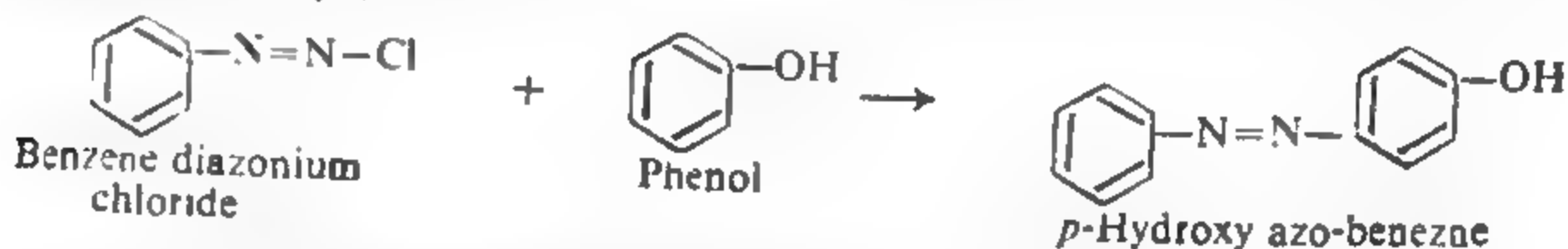
PHENOL



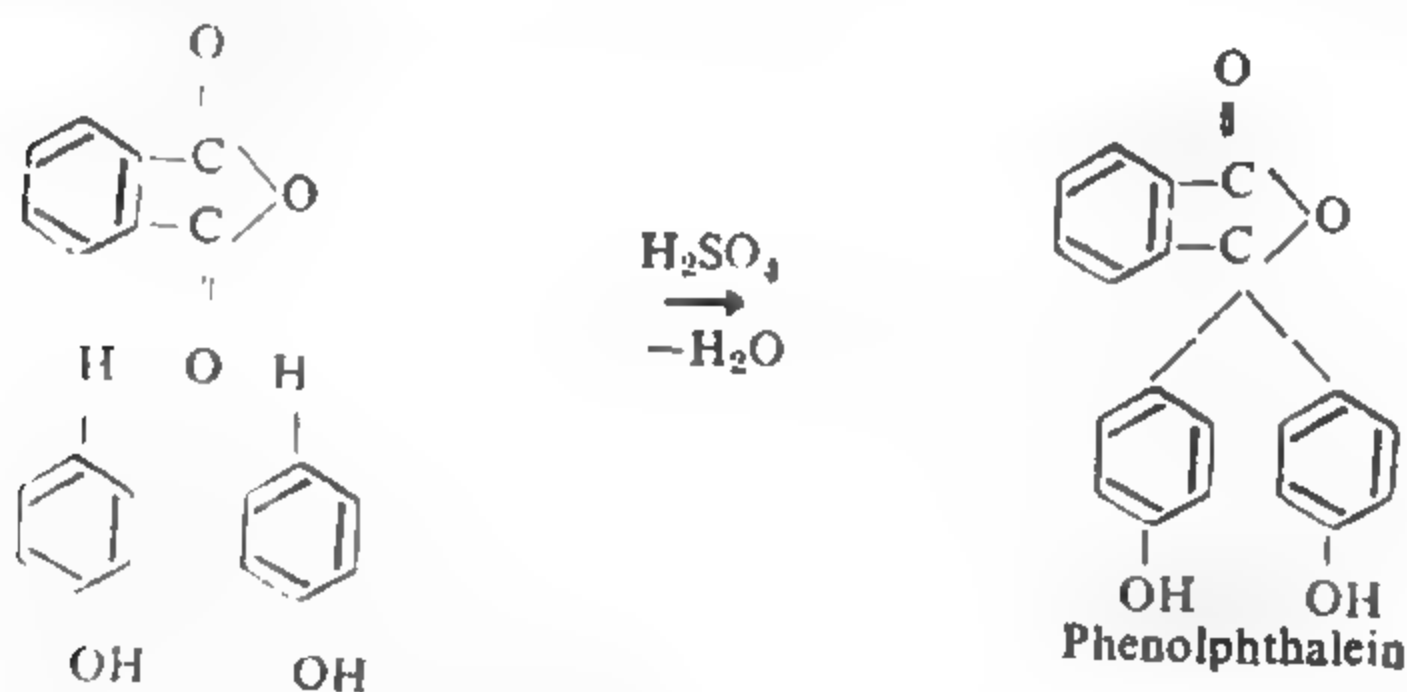
Similar mechanism with CCl_4 will yield salicylic acid.

In actual practice, phenol yields both ortho- and para-hydroxy aldehydes and acids.

3. **Coupling Reaction.** Phenol in alkaline solution condenses with benzene diazonium chloride to yield the corresponding azo compound (a brilliant red dye).

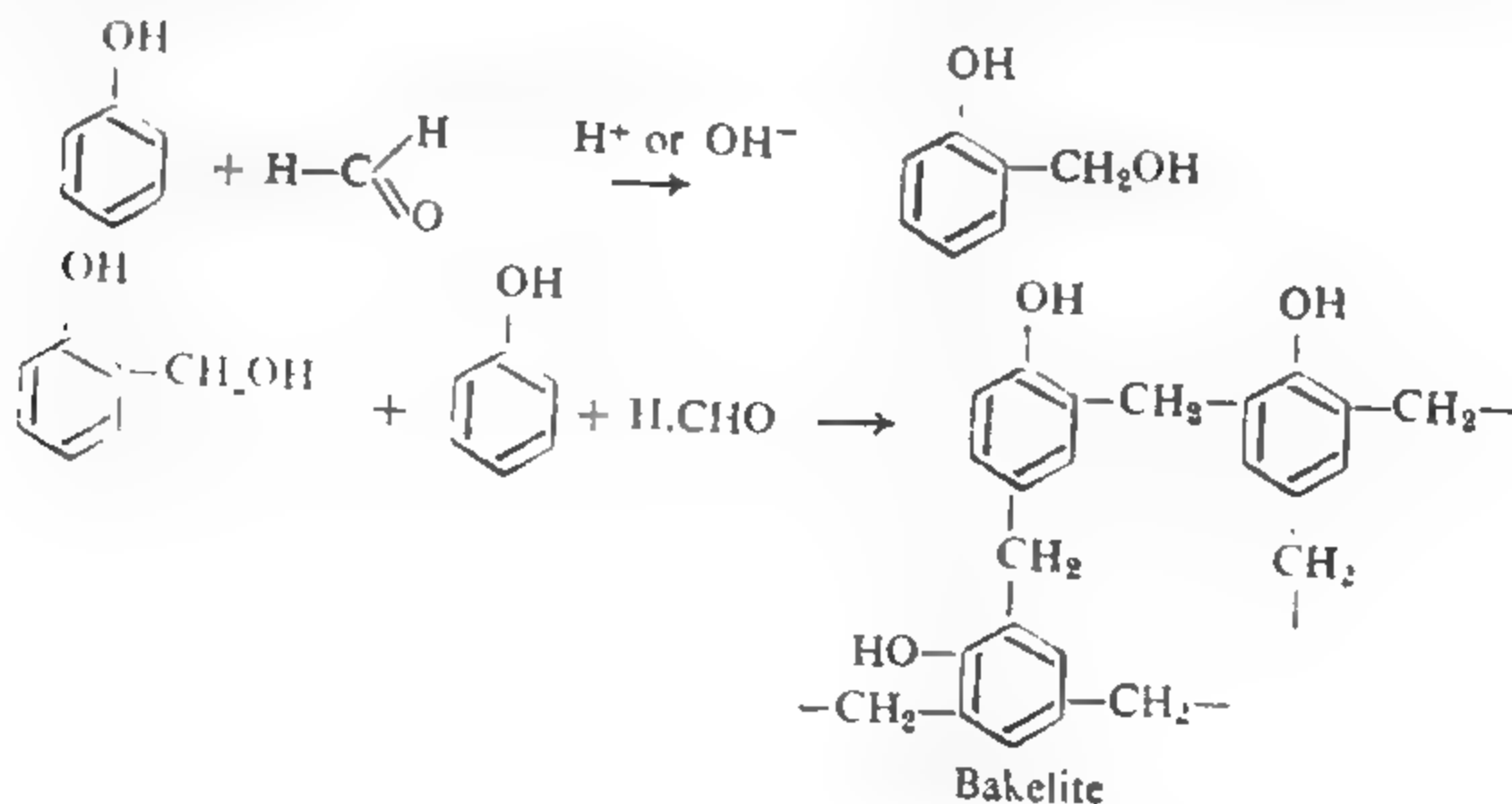


4. **Reaction with phthalic anhydride.** Phenol when heated with phthalic anhydride in the presence of concentrated sulphuric acid, forms phenolphthalein.



As is well-known, phenolphthalein is used as an indicator in acid-alkali titrations, for it is colourless in acidic medium and pink in alkaline solution.

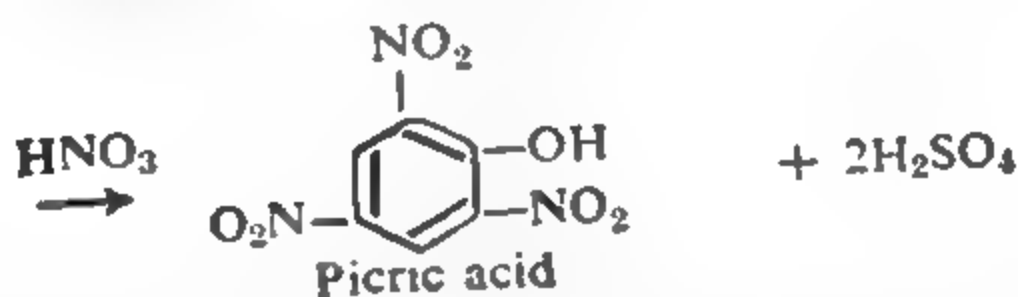
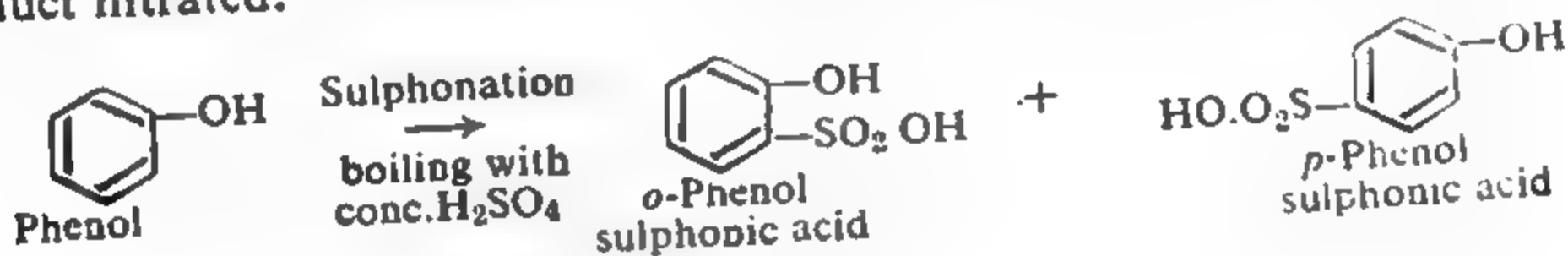
5. **Condensation with formaldehyde.** Phenol condenses with formaldehyde in the presence of acids or alkalies to yield the well-known plastic bakelite.



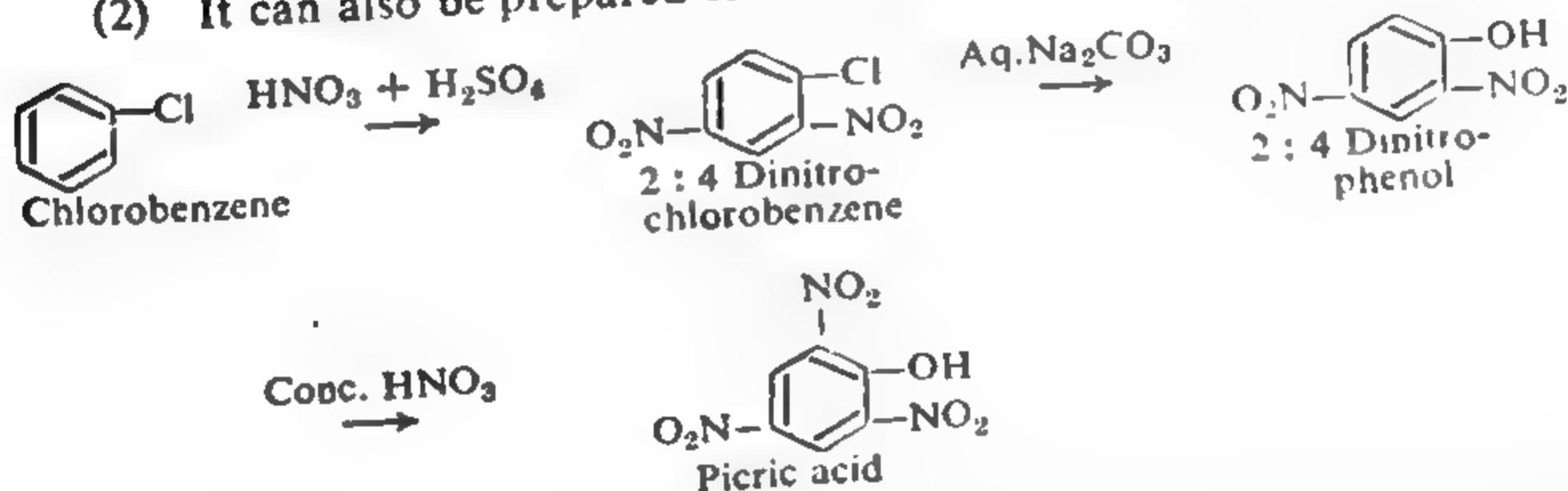
Uses. Phenol is extensively used (i) for the preparation of bakelite plastics (ii) in the manufacture of drugs like salicylic acid, aspirin, salol, phenacetin and compounds like phenolphthalein (iii) in the preparation of picric acid (an explosive and a dye) and dye stuffs (iv) in the preparation of antiseptic solutions, carbolic soaps, etc. A 30% solution is generally used for washing wounds (v) as a solvent (in the form of cyclohexanol) for rubber and nitrocellulose, lacquers and in the manufacture of synthetic fibre, nylon and (vi) as a preservative for ink.

Picric Acid, 2 : 4 : 6 Trinitrophenol, $C_6H_2(OH)(NO_2)_3$

Picric acid is prepared by exhaustive nitration of phenol. It has already been pointed out that the nitration of phenol at room temperature yields *o*- and *p*-nitrophenols and direct nitration of phenol with conc. nitric acid forms picric acid but the yield is very poor. Hence, nitration is carried out in an indirect way. Phenol is first sulphonated and the product nitrated.



(2) It can also be prepared from chlorobenzene as below :



Properties. Picric acid is a brilliant yellow crystalline solid (m.p. 122°), with an extremely bitter taste and hence its name (Greek, *pikros* = bitter). It is only slightly soluble in water, but more so in hot water. It dissolves in alcohol, ether and benzene. As an acid, it is stronger than phenol and decomposes alkali carbonates. It is a mild antiseptic for burns, but is poisonous in character.

With phosphorus pentachloride, it forms the picryl chloride,

$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{Cl}$ (cf. reaction of phenol with PCl_5). With potassium salts, it forms crystalline potassium picrate, $\text{C}_6\text{H}_2(\text{OK})(\text{NO}_2)_3$.

Uses. Picric acid is used (i) as a dyestuff for dyeing woollen and silken fabrics yellow (ii) as an explosive and (iii) as a reagent in laboratory.

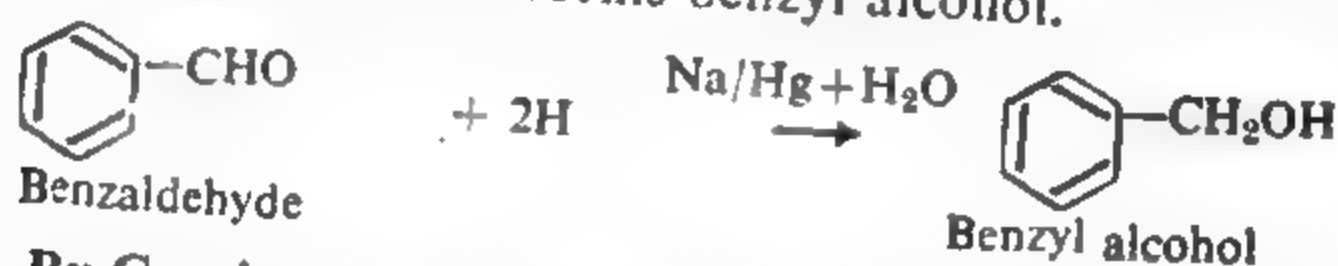
BENZYL ALCOHOL, $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$

Benzyl alcohol occurs free and as its ester with benzoic acid and cinnamic acid, in *Peru tolu balsams*. In the form of its acetate, it has been found to be present in jasmine.

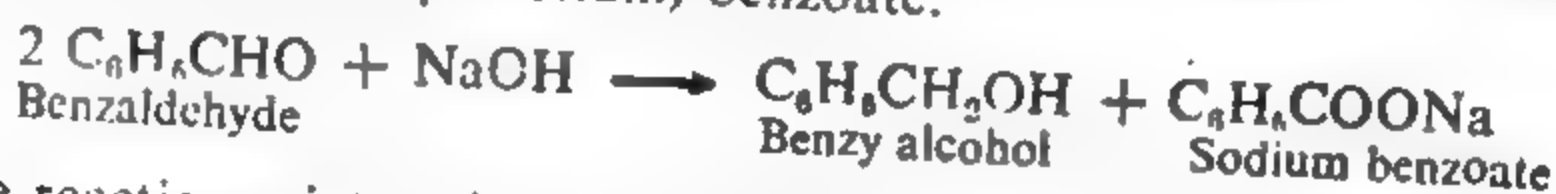
It is a typical representative of aromatic alcohols.

Preparation. Benzyl alcohol can be prepared by the following methods :

(1) **By the reduction of benzaldehyde.** Benzaldehyde on reduction with sodium amalgam and water forms benzyl alcohol.



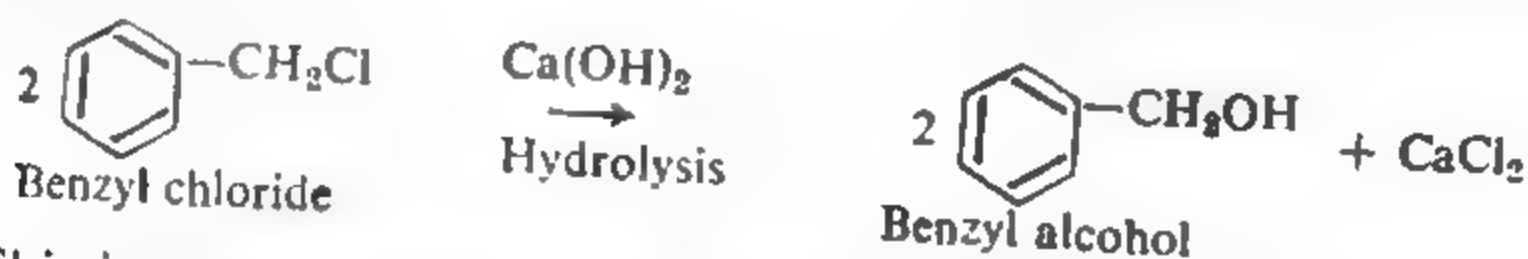
(2) **By Cannizzaro's reaction.** Benzaldehyde when treated with aqueous sodium (or potassium) hydroxide, yields a mixture of benzyl alcohol and sodium (or potassium) benzoate.



The reaction mixture is extracted with ether and the ethereal solution, after drying with anhydrous potassium carbonate, is distilled. The ether distils off and pure benzyl alcohol remains as residue.

This is a very convenient method to prepare benzyl alcohol in laboratory.

(3) **By the hydrolysis of benzyl chloride.** Benzyl chloride is hydrolysed by boiling with milk of lime or sodium carbonate solution, when benzyl alcohol is formed.



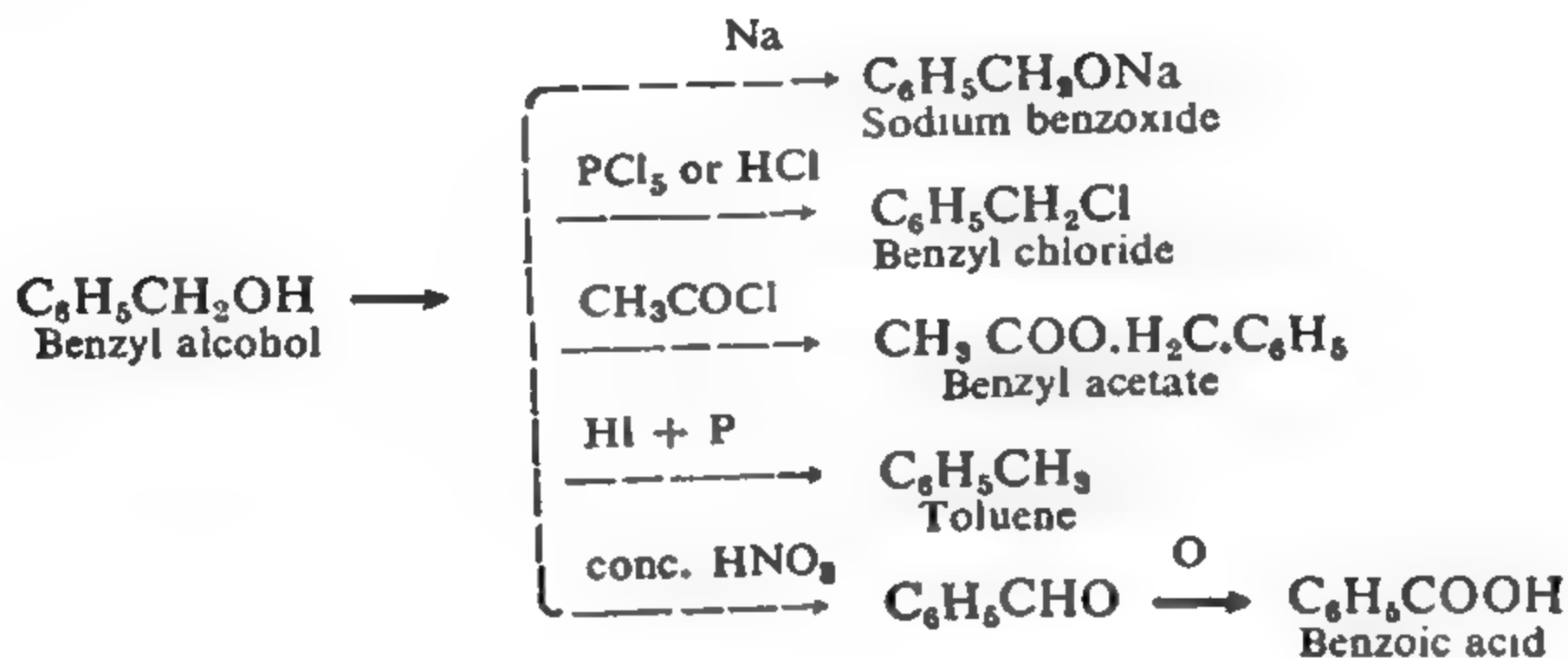
This is a commercial method for the manufacture of benzyl alcohol.

Properties. Benzyl alcohol is a colourless liquid (b. p. 205°), with a pleasant smell. It is sparingly soluble in water, but freely soluble in organic solvents.

Chemically, benzyl alcohol resembles aliphatic alcohols. Thus, it reacts with metallic sodium, phosphorus penta-chloride, hydrochloric acid, sulphuric acid, acetyl chloride and acetic anhydride to form

compounds similar to those formed by ethyl alcohol. It is reduced to toluene on treatment with hydriodic acid and oxidised to benzoic acid on treatment with nitric acid.

Thus



Uses. (1) Benzyl alcohol and its esters, particularly the acetate and benzoate, are used in synthetic perfumes. (2) It finds use in medicine as a mild anaesthetic and as an antiseptic. It is a specific remedy for asthma and whooping cough. (3) It is also used in the manufacture of synthetic resins.

Comparison of Phenol with Aliphatic Alcohols

Points of Resemblance

1. Both phenol and aliphatic alcohols react with sodium metal to give hydrogen.
2. Both react with acetyl chloride and acetic anhydride to form esters.
3. Both react with PCl_5 forming chlorides ($-\text{OH}$ group is replaced by $-\text{Cl}$).
4. Both are reduced to the parent hydrocarbons on heating with zinc dust.
5. Both react with ammonia in the presence of anhydrous zinc chloride to form amines.
6. Sodium salts of both phenol and aliphatic alcohols react with alkyl halides to form ethers.

Points of Difference

1. Phenol is feebly acidic, while aliphatic alcohols are neutral in character. Phenol forms salts with strong alkalies. Alcohols do not react.

2. Phenol is not attacked by halogen acids. Alcohols, on the other hand, react easily forming alkyl halides.

3. Phenol is not easily oxidised. Alcohols are readily oxidised to aldehydes or carboxylic acids.

4. Phenol gives a violet coloration with ferric chloride. Alcohols do not.

5. Phenol gives the typical reactions such as Kolbe's reaction, Liebermann's reaction, Reimer Tiemann's reaction, etc. Alcohols do not give any such reactions.

6. Phenol reacts with halogens forming nuclear substituted derivatives. For instance, with Cl_2 (or Br_2), 2 : 4 : 6 trichloro (or tribromo) phenol is obtained. Aliphatic alcohols are first oxidised to aldehydes and then get halogenated. For instance, with Cl_2 , ethyl alcohol first gives acetaldehyde and then trichloro acetaldehyde (chloral).

7. Phenol reacts with sulphuric acid and nitric acid giving nuclear substituted derivatives. Alcohols, on the other hand, form esters (sulphates and nitrates).

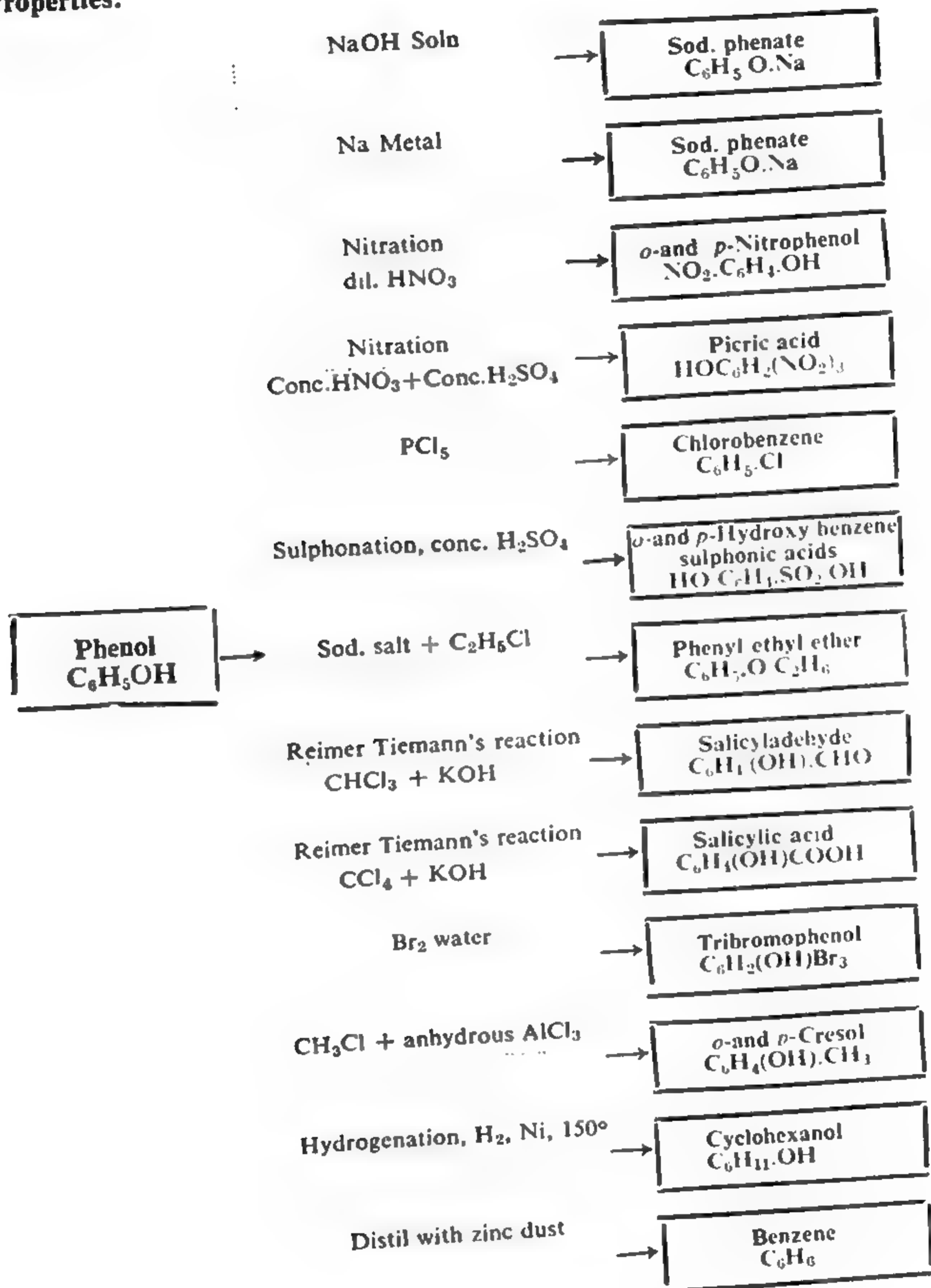
SUMMARY OF TYPICAL MEMBERS

PREPARATION AND PROPERTIES OF PHENOL

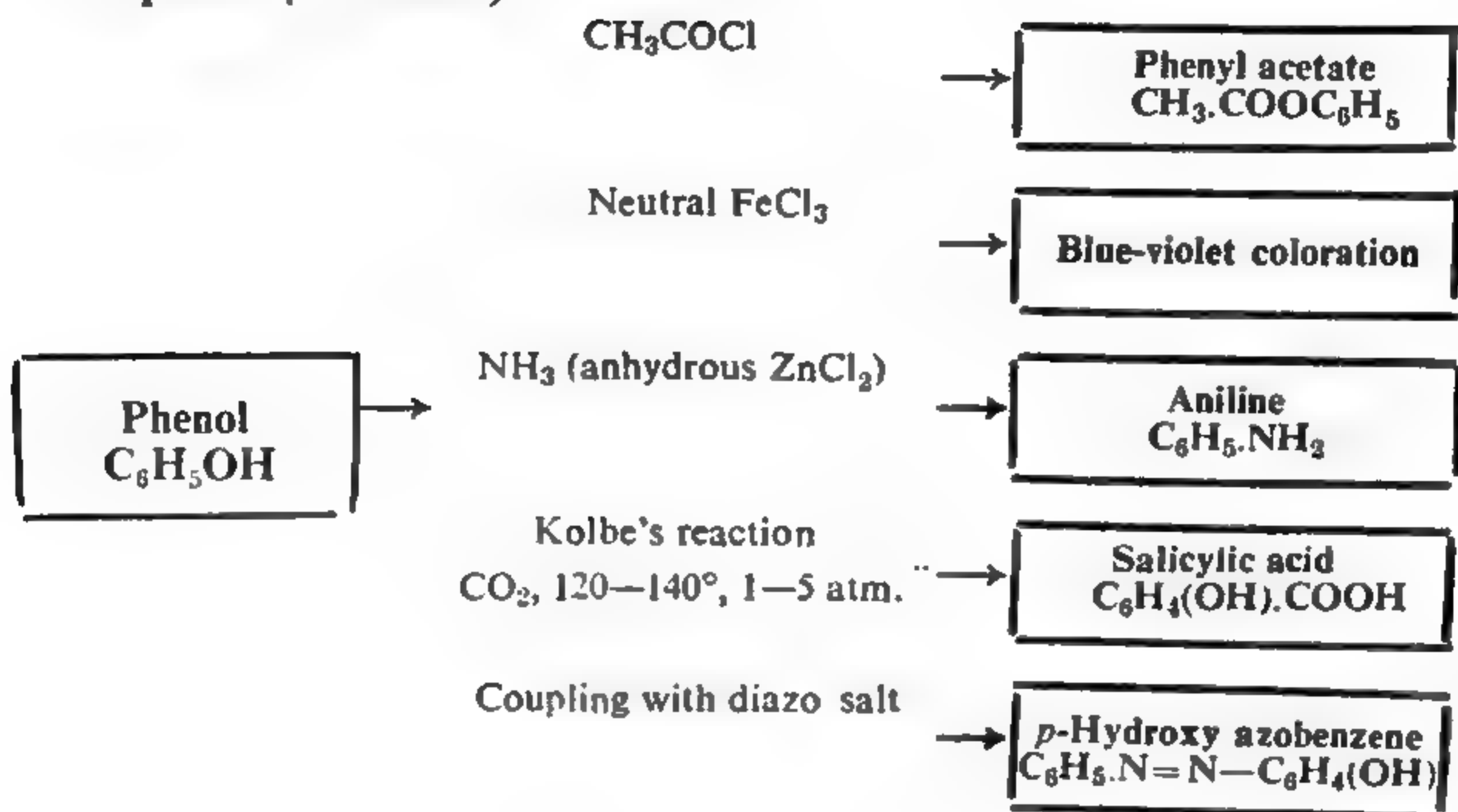
Preparation.

Sod. benzene sulphonate $\text{C}_6\text{H}_5\text{SO}_2\text{ONa}$	NaOH solid, Fuse	→	
Benzene diazonium chloride $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$	Water, 50—60°	→	
Chlorobenzene $\text{C}_6\text{H}_5\text{Cl}$	NaOH, 300°, 200 atms. Cu salt Dow's Process	→	
Salicylic acid $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$	Soda lime, Distil	→	Phenol $\text{C}_6\text{H}_5\text{OH}$
Benzene C_6H_6	Raschig's process	→	
Grignard reagent $\text{C}_6\text{H}_5\text{MgBr}$	O_2 , followed by hydrolysis	→	

Properties.



Properties (continued)



QUESTIONS

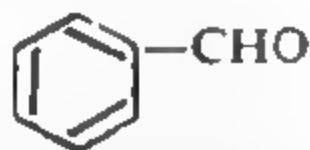
- Describe the commercial preparation of phenol from coal tar. What are its important reactions?
- What are phenols and aromatic alcohols? How do they differ in their chemical behaviour?
- Write short notes on :
(i) Kolbe's Reaction. (ii) Reimer-Tiemann's reaction. (iii) Coupling reaction and (iv) Cannizzaro's reaction.
- How will you obtain phenol from (a) Chlorobenzene (b) Aniline (c) Benzene and (d) Benzene sulphonic acid? Indicate the conditions employed in each case. What are the uses of phenol?
- (a) How does Phenol react with (i) phosphorus pentachloride (ii) KOH (iii) bromine (iv) HNO_3 (v) ferric chloride and (vi) phthalic anhydride.
(b) How is phenol converted into (i) salicylic acid (ii) phenyl acetate (iii) bromine (iv) *p*-hydroxy azobenzene and (v) benzoyl chloride?
- How is benzyl alcohol prepared? What are its characteristic properties and uses?
In what respect does it differ, if at all it does so, from phenol?
- Give the preparation, properties and uses of Picric acid.
- (a) How is phenol isolated from 'Middle oil' fraction of coal tar distillation?
(b) Give four properties involving the hydroxyl group and two properties involving substitution of benzene ring of phenol.
(Panjab Inter 1961 S)
- Give the preparation, properties and uses of : Picric Acid or Salicylic acid.
(Panjab Inter 1961)
- Give two methods of preparation, two reactions similar to and two different from aliphatic alcohols, two uses and two tests of phenol.
(Panjab Inter 1960 S)
- What happens when hydroxy benzene is subjected to :—(i) Friedel Craft's reaction (ii) Reimer Tiemann's reaction and (iii) condensation with phthalic anhydride in presence of conc. H_2SO_4 .
(Panjab Inter 1959 S)
- Give the various stages by which benzene may be converted into phenol. How does phenol react with the following : (a) bromine water (b) a mixture of concentrated nitric acid and sulphuric acid (c) caustic soda and (d) acetyl chloride?
(Panjab Inter 1957)

CHAPTER LII

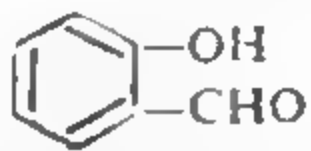
AROMATIC ALDEHYDES AND KETONES

Aromatic Aldehydes Two types of aromatic aldehydes are known :

(i) Those in which aldehydic group is directly attached to the nucleus, e.g.,

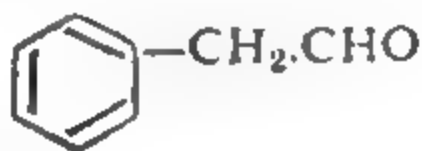


Benzaldehyde



Salicylaldehyde

(ii) Those in which the aldehydic group is attached to the side chain, e.g.,



Phenyl acetaldehyde

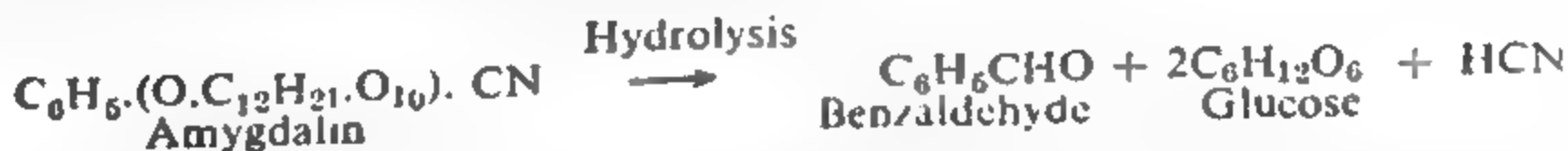
The aldehydes belonging to the first type are true aromatic aldehydes, and those belonging to the second type may better be regarded as aryl-substituted aliphatic aldehydes.

BENZALDEHYDE, $C_6H_5 \cdot CHO$

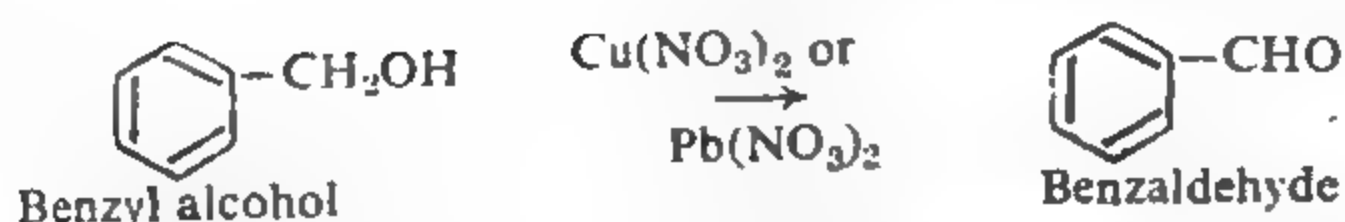
Benzaldehyde is the most important member of the aromatic aldehydes. It occurs as glucoside, *amygdalin*, in bitter almonds, the kernel of peaches, apricots, and cherry. Therefore, it is also known as *oil of bitter almonds*. Oil of bitter almonds contains 96—98% of benzaldehyde.

Preparation. Benzaldehyde can be obtained by the following methods :

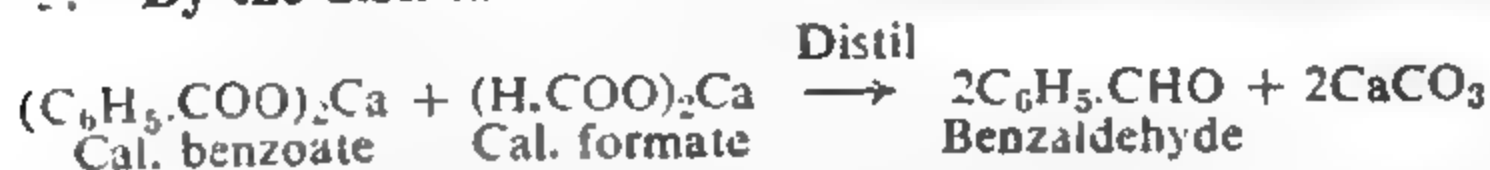
1. By the hydrolysis of amygdalin. The glucoside, amygdalin, occurring in bitter almonds, on hydrolysis with dilute hydrochloric acid or by the enzyme *emulsin*, yields benzaldehyde.



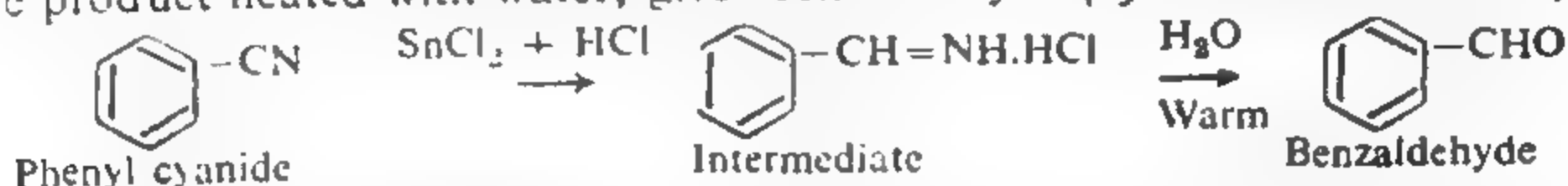
2. **By the oxidation of benzyl alcohol.** Benzyl alcohol on oxidation with dilute nitric acid or with lead or copper nitrate yields benzaldehyde.



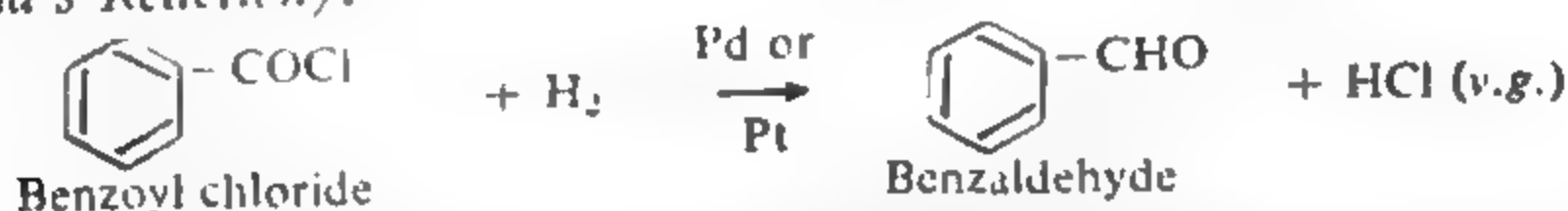
3. By the distillation of calcium benzoate with calcium formate.



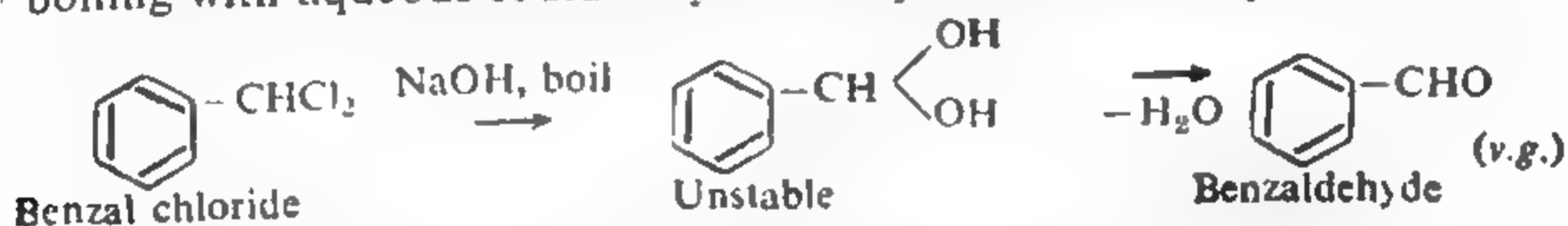
4. By the reduction of phenyl cyanide. Phenyl cyanide when reduced with stannous chloride and hydrochloric acid in ethereal solution and the product heated with water, gives benzaldehyde (*cf. Mendius Reaction*).



5. By the reduction of benzoyl chloride. Benzoyl chloride may be reduced by hydrogen in the presence of platinum or palladium deposited over barium sulphate at 120–150° to yield benzaldehyde (*cf. Rosenmund's Reaction*).

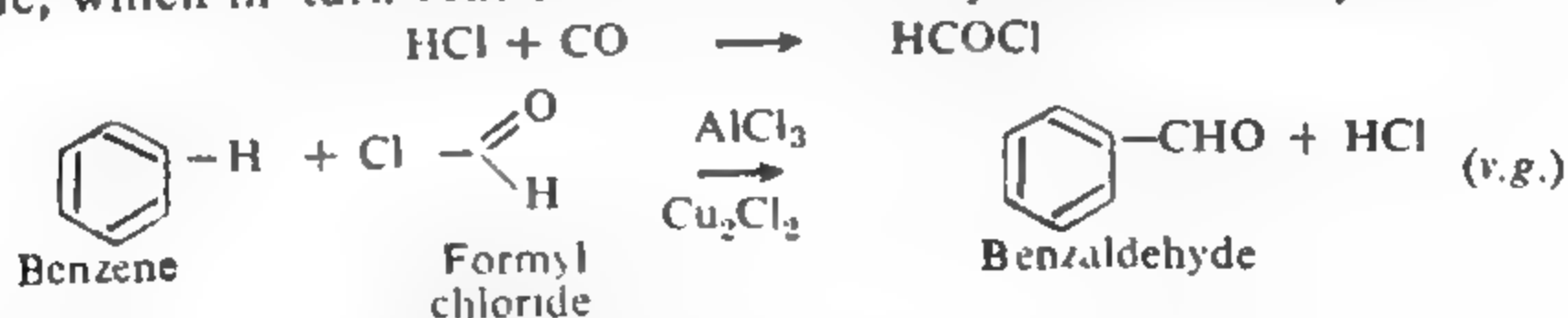


6. By the hydrolysis of benzal chloride. Benzal chloride on hydrolysis by boiling with aqueous sodium hydroxide yields benzaldehyde.

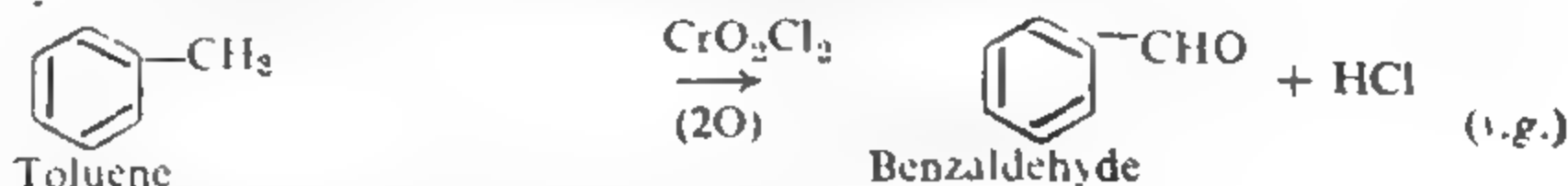


Benzal chloride for the purpose is obtained from toluene.

7. By Gatterman-Koch's reaction. This is just a modified form of Friedel-Craft's reaction. A mixture of hydrogen chloride and carbon monoxide is passed through a solution of benzene in ether or nitrobenzene containing anhydrous cuprous chloride and anhydrous aluminium chloride at 40–45° and 70 atmospheres pressure. Probably formyl chloride is first formed by interaction between hydrogen chloride and carbon monoxide, which in turn reacts with benzene to yield benzaldehyde.



(8) By controlled oxidation of toluene. Toluene, on warming with chromyl chloride, gets oxidised to benzaldehyde.



This is known as Etard's reaction.

A mixture of manganese dioxide and sulphuric acid has also been used for the oxidation of toluene to benzaldehyde.

The oxidation may also be brought about by passing toluene vapour mixed with air over heated vanadium pentoxide.

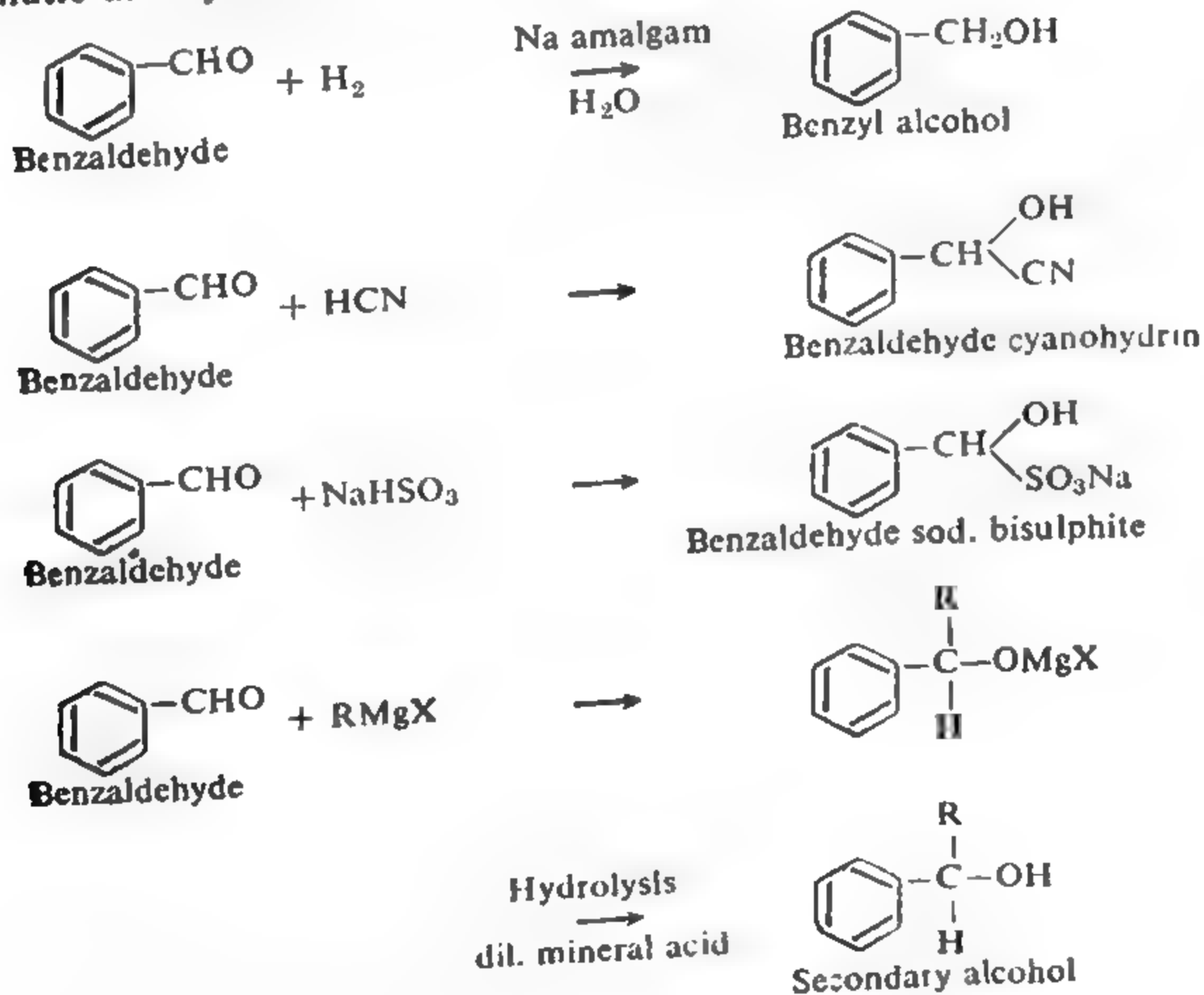
Physical Properties. Benzaldehyde is a colourless liquid (b.p. 179°) with an odour resembling that of bitter almonds. It is volatile in steam. It is only sparingly soluble in water, but soluble in organic solvents like ethyl alcohol and ether.

Chemical Properties. Chemically, benzaldehyde is quite reactive and undergoes a number of reactions which can be studied under the following heads :

(i) Reactions of aldehydic group (ii) Reactions of aldehydic group peculiar to benzaldehyde (iii) Reactions of aromatic nucleus.

(i) Reactions of the Aldehydic Group.

(a) Addition reactions. Benzaldehyde adds up hydrogen, hydrogen cyanide, sodium bisulphite and Grignard reagents, in the same manner as aliphatic aldehydes do.

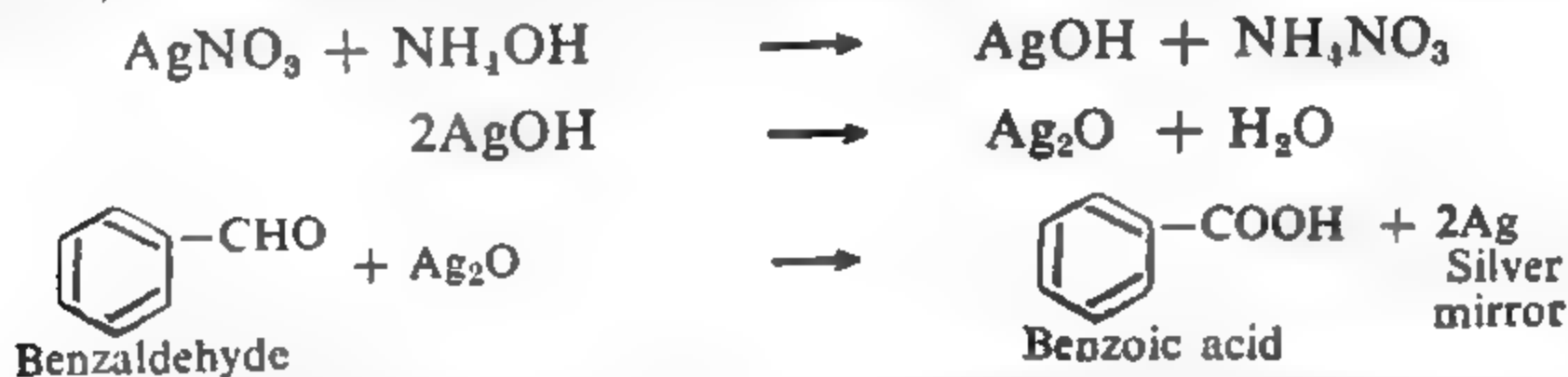


(b) Oxidation. Benzaldehyde is very easily oxidised (even by the atmospheric oxygen) to benzoic acid.



It is due to this reason that the outside of the stopper of a bottle containing benzaldehyde is usually coated with crystals of benzoic acid.

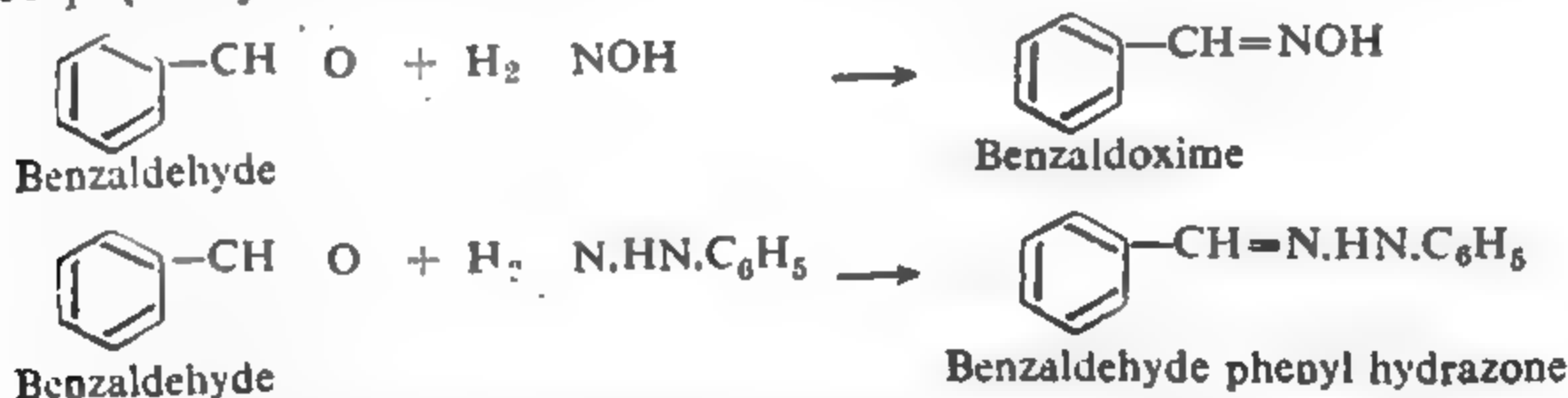
(c) **Reducing action.** Benzaldehyde reduces ammoniacal silver nitrate solution, but not Fehling solution (*difference from aliphatic aldehydes*).



(d) **Replacement reactions.** (1) **With phosphorus pentachloride.** Benzaldehyde on treatment with phosphorus pentachloride yields benzal chloride by replacement of the oxygen atoms.



(2) **With hydroxylamine and phenylhydrazine.** Benzaldehyde reacts with these reagents to yield the corresponding oxime and phenylhydrazone respectively.



(e) **Schiff's reaction.** Benzaldehyde restores the pink colour of Schiff's reagent (rosaniline hydrochloride solution decolorised with sulphur dioxide).

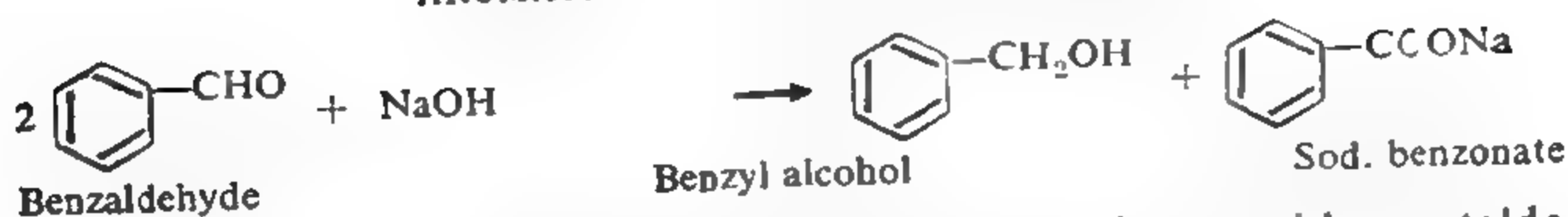
(ii) **Reactions of the Aldehydic Group peculiar to Benzaldehyde.**

1. **Condensation with ammonia.** Benzaldehyde differs from aliphatic aldehydes in its reaction with ammonia as it does not form an addition compound with ammonia, but forms a complex compound hydrobenzamide, $(\text{C}_6\text{H}_5\text{CH})_3\text{N}_2$

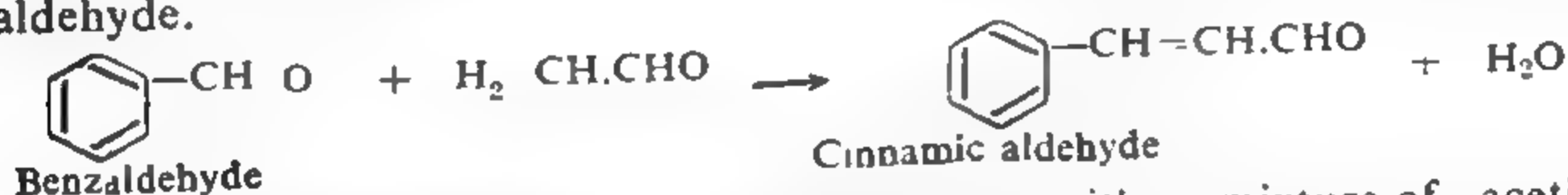


Formaldehyde reacts similar to benzaldehyde.

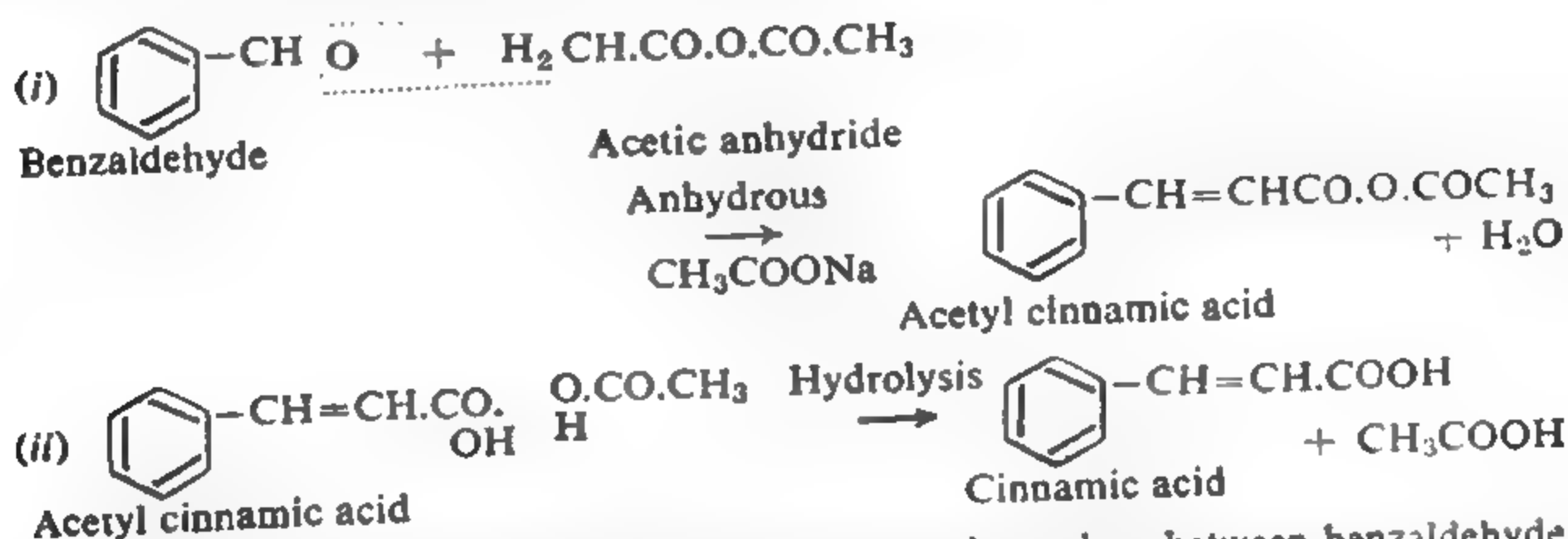
2. **Cannizzaro's reaction.** Benzaldehyde undergoes Cannizzaro's reaction in the presence of dilute caustic soda solution to yield benzyl alcohol and benzoic acid.



3. **Claisen's condensation.** Benzaldehyde condenses with acetaldehyde in the presence of dilute sodium hydroxide solution to give cinnamic aldehyde.



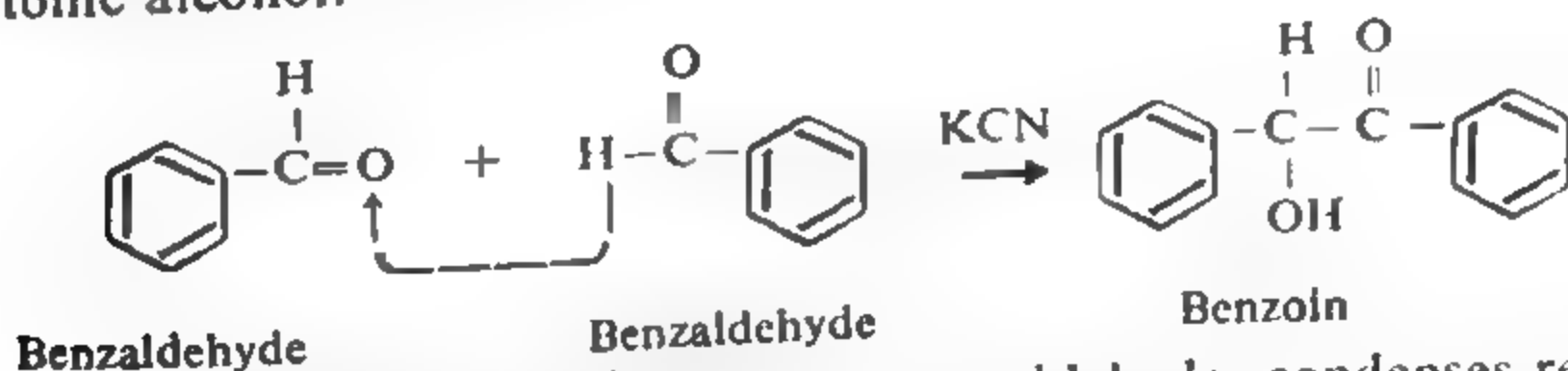
4. **Perkin's reaction.** Benzaldehyde reacts with a mixture of acetic anhydride and anhydrous sodium acetate to form acetyl cinnamic acid, which on hydrolysis yields cinnamic acid.



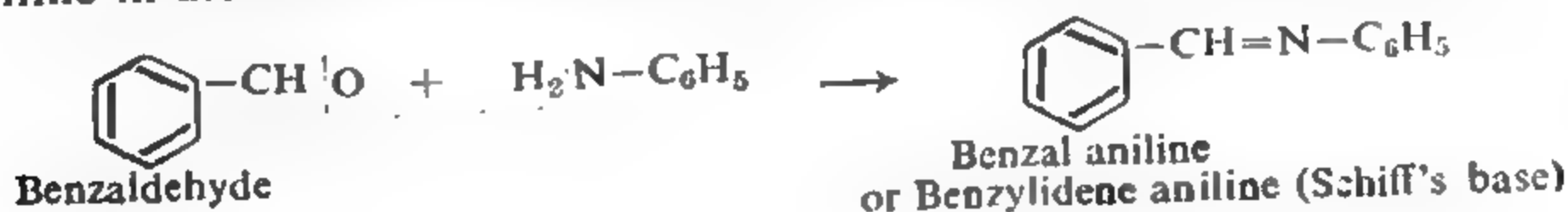
Earlier, it was believed that the condensation takes place between benzaldehyde and anhydrous sod. acetate, acetic anhydride acting as the condensing reagent. But it has now been definitely established that acetic anhydride condenses and anhydrous sod. acetate is the condensing reagent.

The reaction is carried out by refluxing benzaldehyde, acetic anhydride and anhydrous sodium acetate in a round bottomed flask at 180° for 8 hours and pouring the reaction mixture in water and neutralising with sodium carbonate. Any unreacted benzaldehyde is steam-distilled. The remaining solution on acidification precipitates cinnamic acid.

5. **Benzoin condensation.** When benzaldehyde in alcohol solution is refluxed with potassium cyanide for 30 minutes, it forms benzoin, a ketonic alcohol.

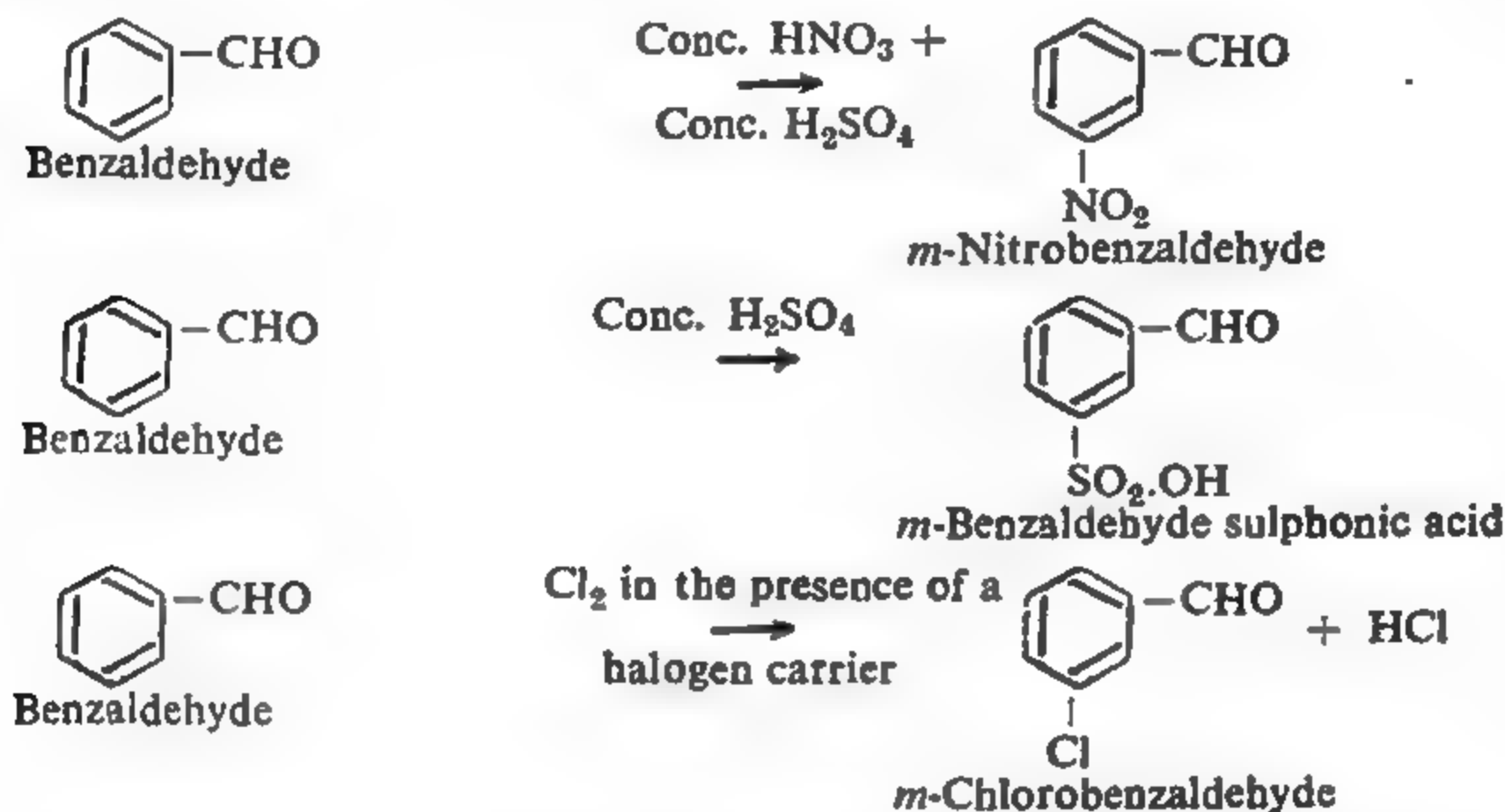


6. **Condensation with aniline.** Benzaldehyde condenses readily with aniline in alcoholic solution to give benzylidene aniline or *Schiff's base*.



(iii) Reactions of Aromatic Nucleus

Benzaldehyde undergoes the usual substitution reactions of the benzene nucleus. It undergoes nitration, sulphonation and halogenation (*in the presence of halogen carrier only*), the main products being the meta-derivatives.



It may be of interest to note that the aldehydic group is not oxidised on treatment with concentrated nitric acid. Instead, nuclear substitution takes place.

If chlorine is passed into *boiling* benzaldehyde, in the *absence* of any halogen carrier, benzoyl chloride is formed.



Uses. 1. Benzaldehyde is used as a flavouring agent.

2. It is used for synthesising important chemicals like cinnamic aldehyde, cinnamic acid, etc.

3. It is an important intermediate in the manufacture of dyes like malachite green and rosaniline.

Salicylaldehyde, o-Hydroxybenzaldehyde, C₆H₄.(OH)CHO

Salicylaldehyde occurs in the oil of *meadow sweet* as glycoside.

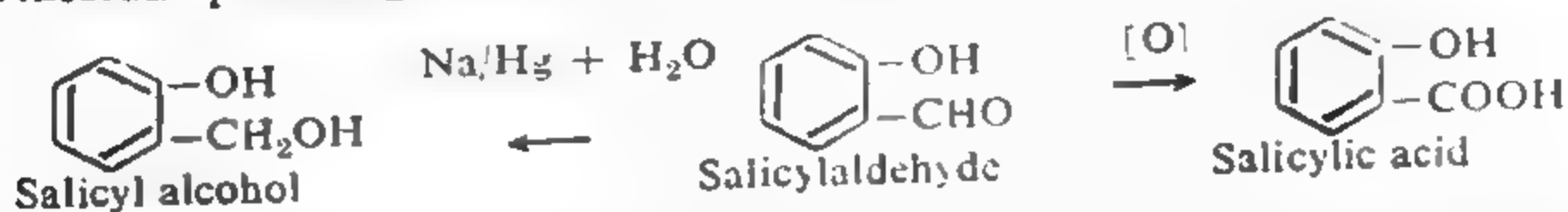
It is usually prepared by *Reimer-Tiemann's reaction*, i.e., by refluxing phenol, chloroform and aqueous caustic potash at 60–70° for nearly two hours.



*Actually, a mixture of *o*- and *p*-hydroxy benzaldehydes is obtained from which *o*-hydroxy benzaldehyde (salicylaldehyde) is separated by steam distillation.

The reaction mixture is acidified and steam-distilled. Salicylaldehyde distils over and is purified through its sodium bisulphite compound.

Properties. Salicylaldehyde is a colourless liquid (b.p. 197°) with a pleasant smell. It is insoluble in water, but dissolves in caustic soda solution. Salicylaldehyde shows the usual properties of phenol as well as aldehyde, for instance, on reduction with sodium amalgam and water, it yields *o*-hydroxy benzyl alcohol (salicyl alcohol), while alkaline potassium permanganate oxidises it to salicylic acid.



With FeCl_3 , it gives an intense violet coloration. However, it does not reduce Fehling solution, neither restores the colour of Schiff's reagent, but it reduces ammoniacal silver nitrate forming a silver mirror (see benzaldehyde).

Salicylaldehyde is used as an intermediate in the preparation of coumarin.

Comparison of Benzaldehyde with Acetaldehyde

Common Properties.

1. Both benzaldehyde and acetaldehyde form addition products with H_2 , HCN and NaHSO_3 .
2. Both form condensation products with hydroxylamine, hydrazine and phenyl hydrazine.
3. Both react with PCl_5 giving dichloro derivatives.
4. Both are readily oxidised to give acids.
5. Both reduce ammoniacal solution of silver nitrate to metallic silver.
6. Both respond to Schiff's reaction.

Different Properties.

1. Benzaldehyde does not reduce Fehling solution. Acetaldehyde reduces Fehling solution to red cuprous oxide.
2. Benzaldehyde reacts with ammonia giving hydrobenzamide. Acetaldehyde, on the other hand, forms addition product, acetaldehyde-ammonia.
3. Benzaldehyde reacts with aqueous alkalis giving benzyl alcohol and alkali salt of benzoic acid (*Cannizzaro's reaction*). Acetaldehyde, on the other hand, forms a yellowish brown resinous product.
4. Benzaldehyde does not undergo polymerisation. Acetaldehyde readily polymerises to give para-aldehyde.
5. Benzaldehyde reacts with nitric acid and sulphuric acid giving

nuclear substituted compounds. Acetaldehyde, on the other hand, undergoes oxidation when treated with nitric acid and polymerisation when treated with sulphuric acid.

AROMATIC KETONES

Aromatic ketones fall under two categories :

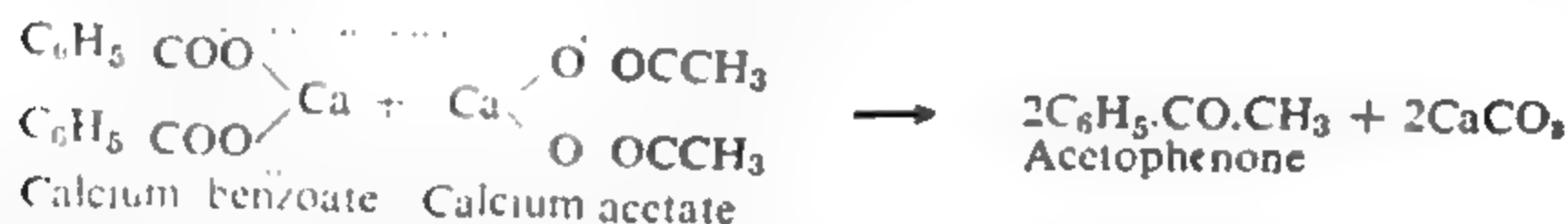
(i) **Aryl alkyl type**, in which an alkyl group and an aryl group are linked to the carbonyl group ($>C=O$), e.g., methyl phenyl ketone or *acetophenone*, $C_6H_5.CO.CH_3$.

(ii) **Purely aromatic type**, in which both the groups linked to the carbonyl group are aryl ones, e.g., diphenyl ketone, or *benzophenone*, $C_6H_5.CO.C_6H_5$.

Both the types of aromatic ketones resemble aliphatic ketones in their methods of preparation and properties except that they do not form the bisulphite compound and show typical reactions of the benzene nucleus.

ACETOPHENONE, METHYL PHENYL KETONE, $C_6H_5.CO.CH_3$

Acetophenone can be prepared by any of the methods for the preparation of ketones. For instance, it may be prepared by distilling a mixture of calcium benzoate and calcium acetate.



(2) It may also be prepared by the interaction of benzene with acetyl chloride in the presence of anhydrous aluminium chloride (*Friedel-Craft's reaction*).

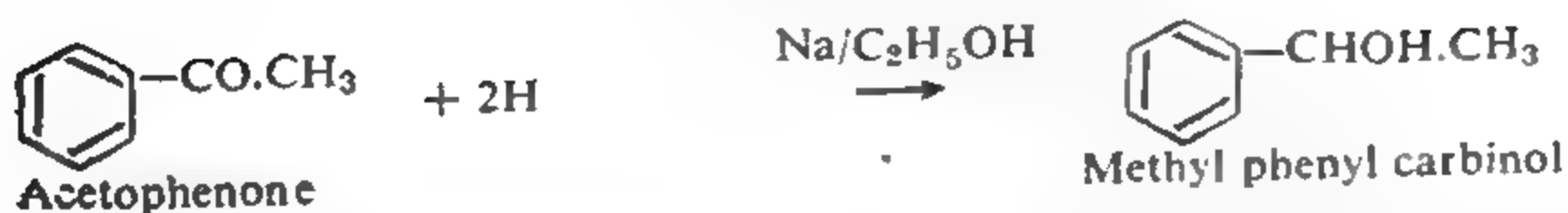


Physical Properties It is a colourless, pleasant smelling crystalline solid, m.p. 20° , b.p. 201° . It is volatile in steam.

Chemical Properties Acetophenone resembles acetone in most of its chemical properties. The properties can be studied under the heads : (i) addition (ii) substitution (iii) oxidation and (iv) reactions of benzene nucleus.

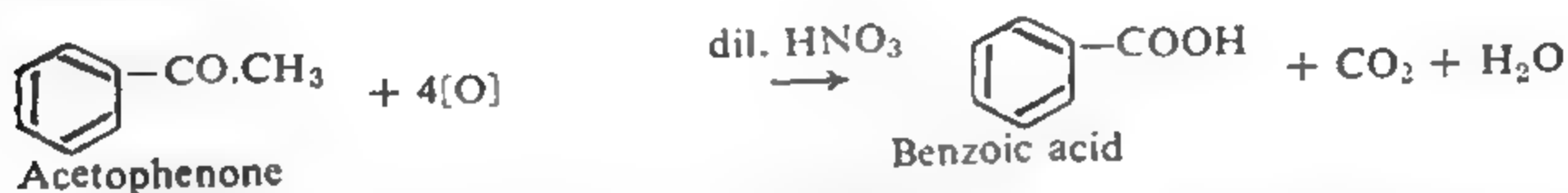
1. **Addition reactions.** It adds up hydrogen cyanide and hydrogen to yield the cyanohydrin and the secondary alcohol respectively.





However, it does not react with sodium bisulphite.

2. **Oxidation.** As might be expected, the side chain —CO.CH_3 is oxidised to the carboxyl group, when acetophenone is heated with dilute nitric acid.



Cold alkaline potassium permanganate, however, forms benzoyl formic acid ($\text{C}_6\text{H}_5\text{CO.COOH}$).

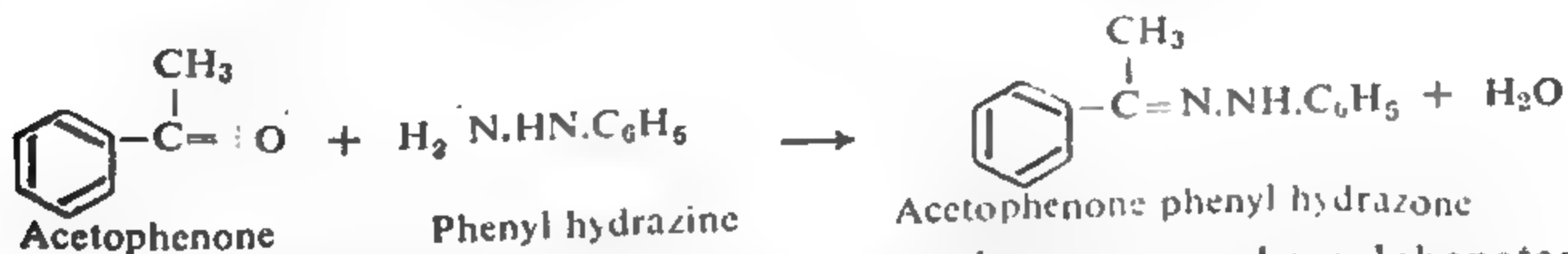
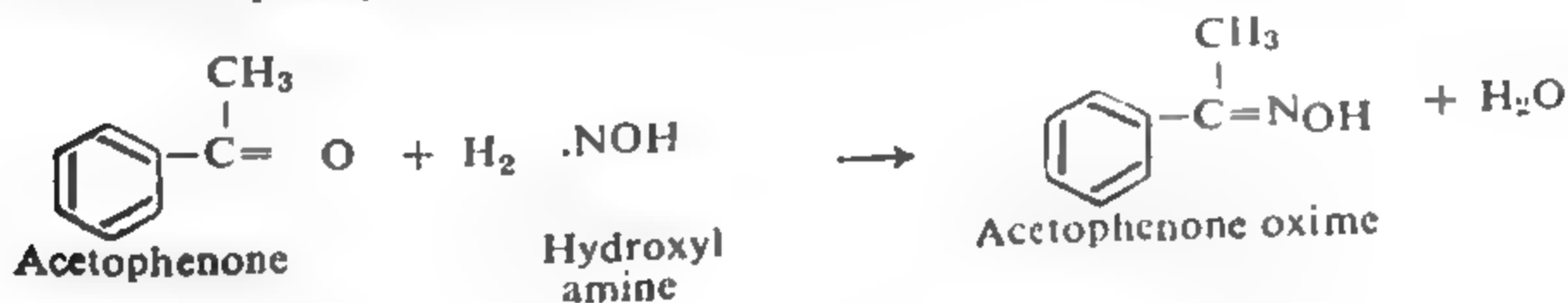


3. **Substitution reactions.** Acetophenone undergoes a number of substitution reactions. For example,

(i) With phosphorus pentachloride, the oxygen of the carbonyl group is replaced by two chlorine atoms.

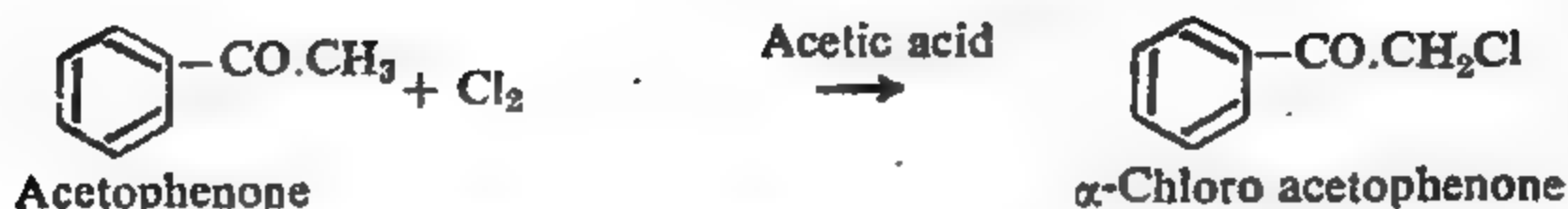


(ii) With hydroxylamine and phenyl hydrazine, the corresponding oxime and phenyl hydrazone are formed.



4. **Reactions of benzene nucleus.** Acetophenone can be sulphonated and nitrated in the usual way, when chiefly the meta compounds are formed.

However, on chlorination, α -chloro acetophenone, $\text{C}_6\text{H}_5\text{CO.CH}_2\text{Cl}$ is formed.

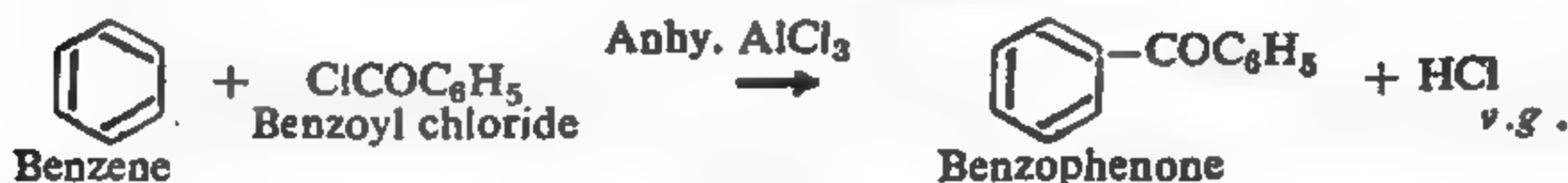


Uses. Acetophenone is used as a hypnotic (sleep-inducing) drug under the name '*hypnone*'. It is also used in perfuming soaps.

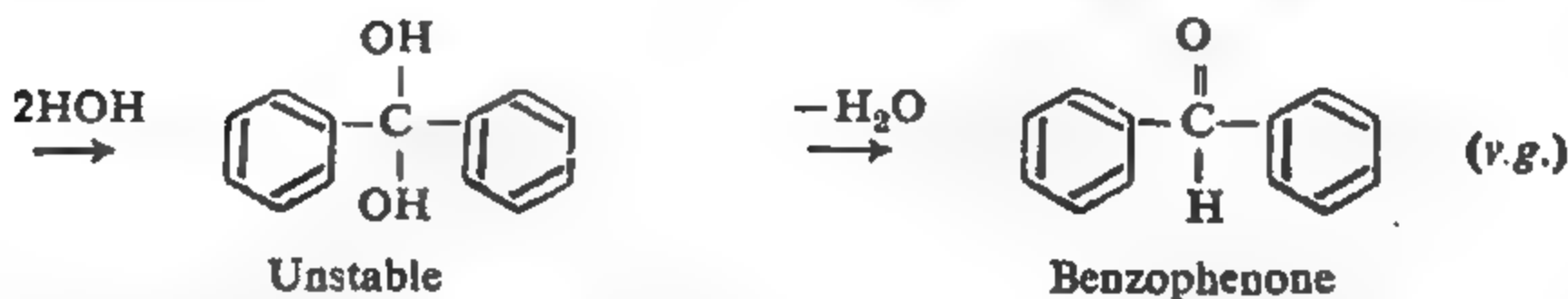
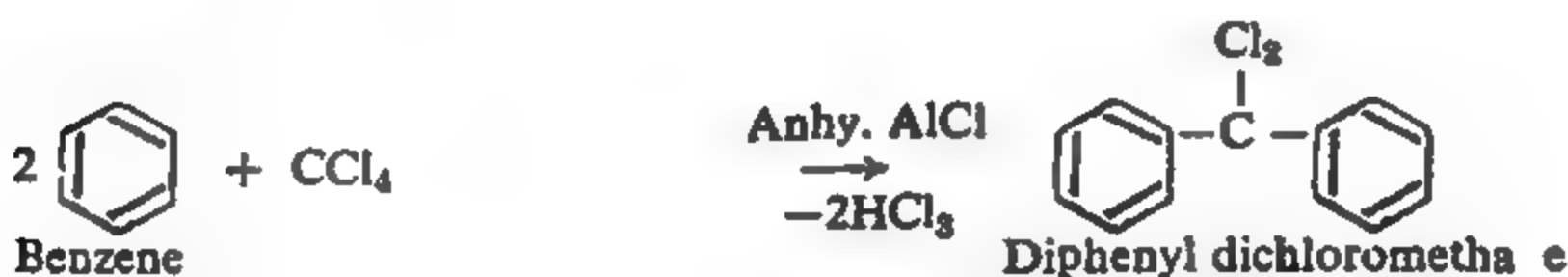
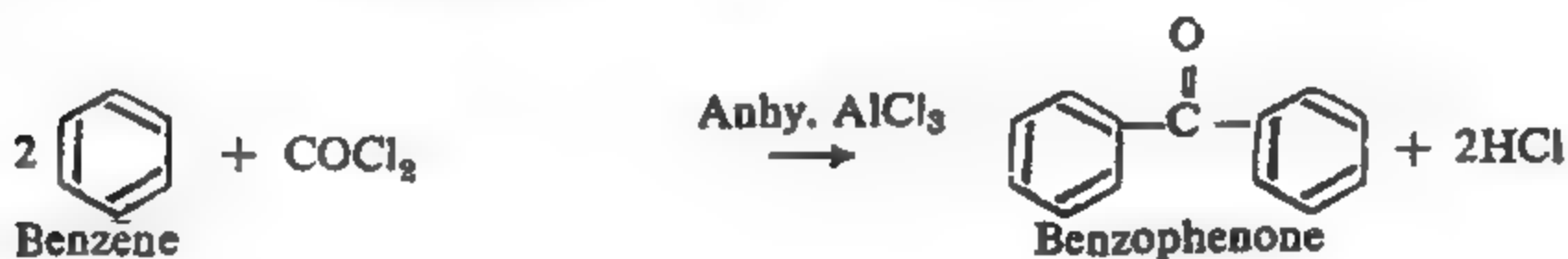
Benzophenone, Diphenyl ketone, $\text{C}_6\text{H}_5\text{CO.C}_6\text{H}_5$. Benzophenone or diphenyl ketone is obtained by distilling calcium benzoate.



It may also be prepared by Friedel-Craft's reaction.

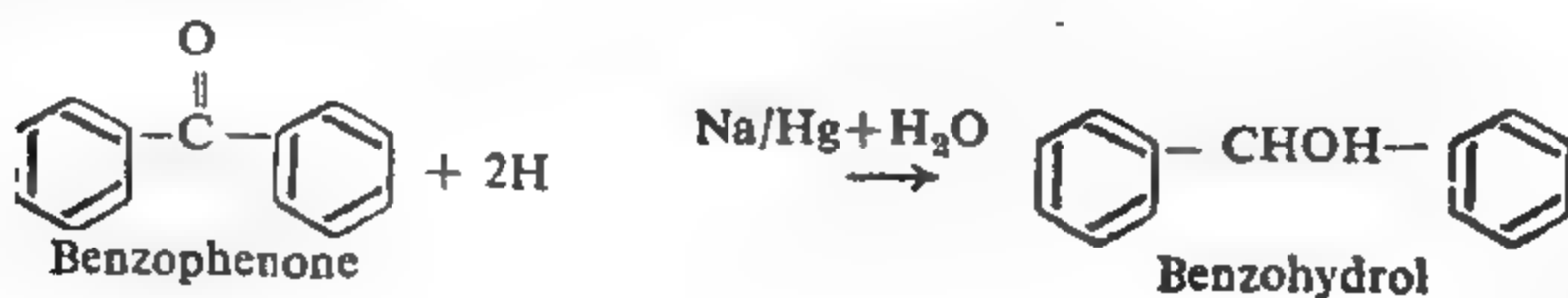


When needed on a commercial scale, the benzoyl chloride is replaced by carbonyl chloride or carbon tetrachloride.

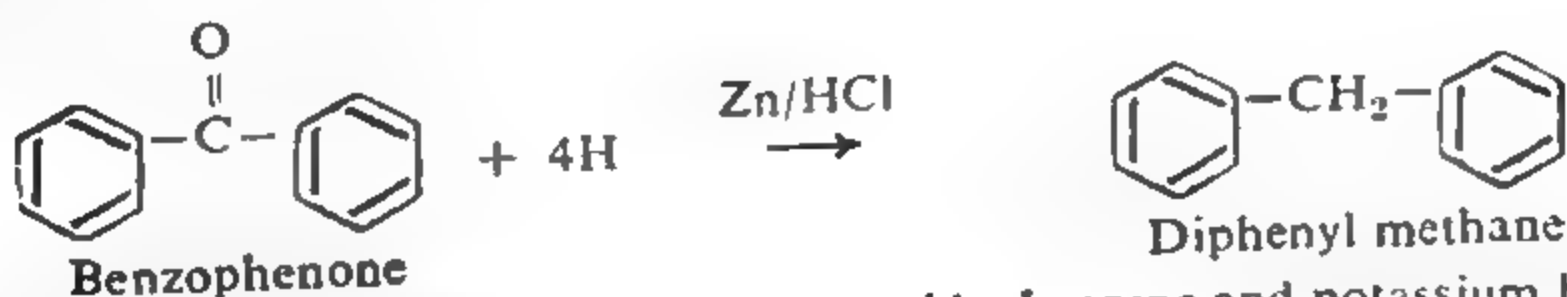


Properties. Benzophenone is a colourless pleasant smelling crystalline solid (m.p. 49°). It is insoluble in water, but soluble in alcohol and ether.

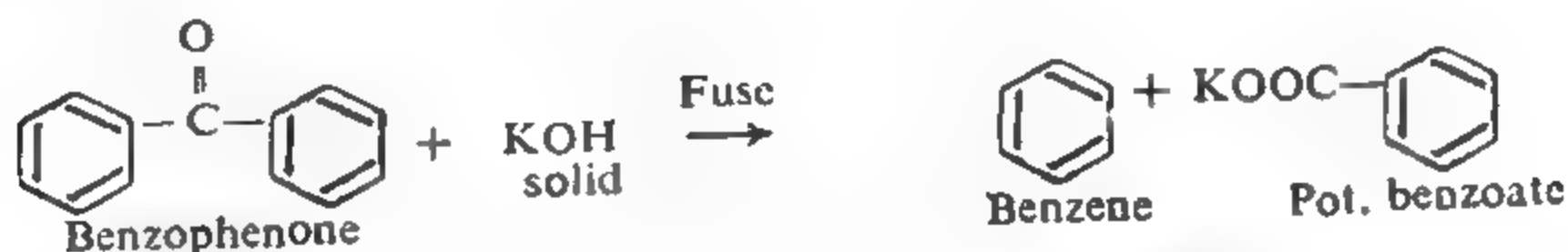
Chemically, it shows reactions very similar to acetophenone. For example, on reduction with sodium amalgam and water, it forms benzohydrol or diphenyl carbinol, $\text{C}_6\text{H}_5\text{CH(OH).C}_6\text{H}_5$.



When reduced with zinc and hydrochloric acid or distilled with zinc dust, diphenyl methane is obtained.

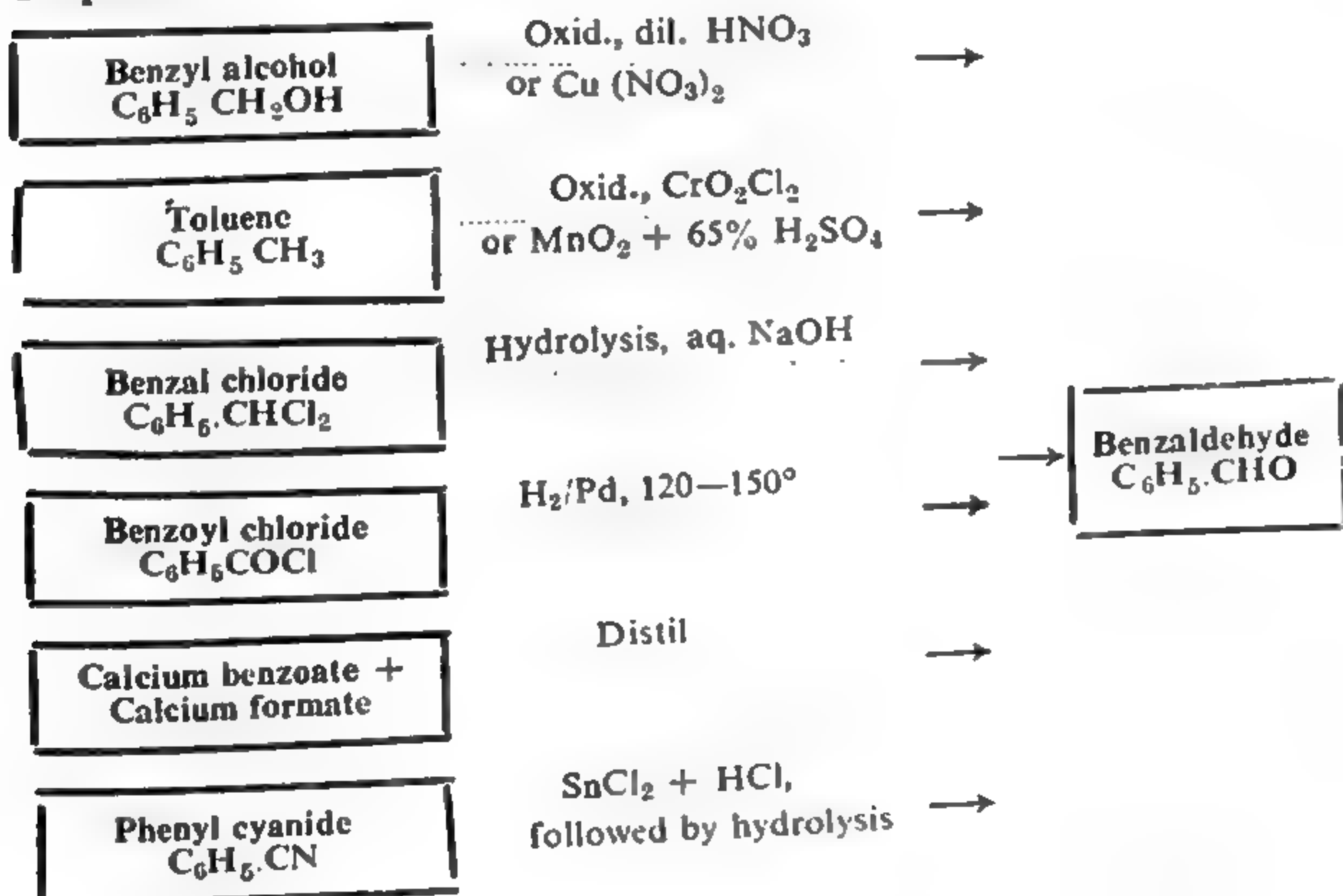


When fused with solid potassium hydroxide, benzene and potassium benzoate are formed.

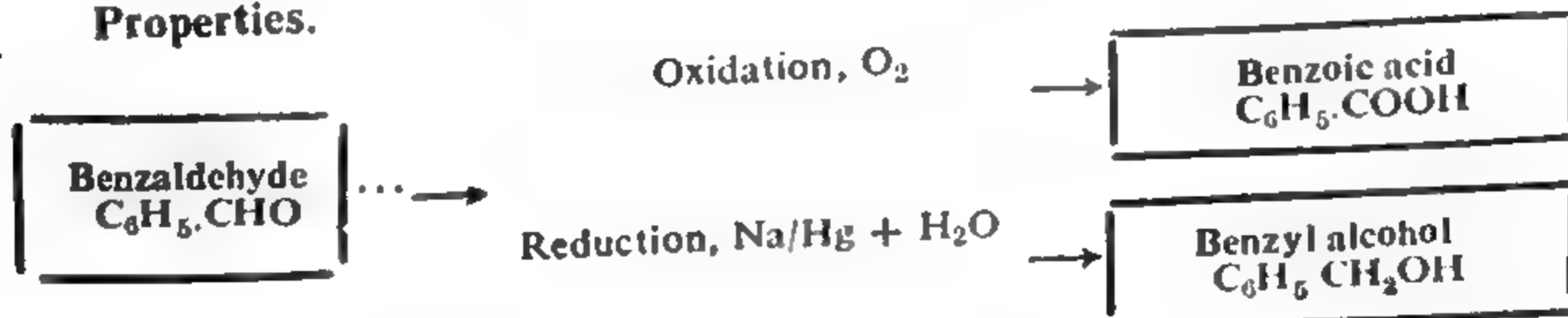


SUMMARY OF A TYPICAL MEMBER PREPARATION AND PROPERTIES OF BENZALDEHYDE

Preparation.



Properties.



Properties. (Contd.)

Benzaldehyde $C_6H_5 \cdot CHO$	HCN	Cyanohydrin $C_6H_5 \cdot CH(OH)CN$
	$NaHSO_3$	Bisulphite compound $C_6H_5 \cdot CH(OH)SO_3Na$
	NH_2OH	Benzaldoxime $C_6H_5 \cdot CH=N \cdot OH$
	$C_6H_5 \cdot NHNH_2$	Phenyl hydrazone $C_6H_5 \cdot CH=N \cdot C_6H_5$
	NH_3	Hydrobenzamide $(C_6H_5 \cdot CH)_3N_2$
	KCN, reflux	Benzoin $C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5$
	Aniline, dil. NaOH	Benzal-aniline $C_6H_5 \cdot CH=N \cdot C_6H_5$
	NaOH (excess) Cannizzaro's reaction	Benzyl alcohol + Benzoic acid
	PCl_5	Benzal chloride $C_6H_5 \cdot CHCl_2$
	CH_3CHO dil. NaOH	Cinnamic aldehyde $C_6H_5 \cdot CH=CH \cdot CHO$
	$(CH_3CO)_2O$, Anhy. CH_3COONa	Cinnamic acid $C_6H_5 \cdot CH=CH \cdot COOH$
	Conc. H_2SO_4	<i>m</i> -Benzaldehyde sul. acid $C_6H_4(CHO) \cdot SO_2 \cdot OH$
	Conc. HNO_3 , conc. H_2SO_4	<i>m</i> -Nitro benzaldehyde $C_6H_4 \cdot (NO_2) \cdot CHO$
	Cl_2 , boiling	Benzal chloride $C_6H_5 \cdot CHCl_2$

QUESTIONS

1. How many types of aromatic aldehydes exist? What is the main structural and chemical difference between these types? Illustrate your answer with suitable examples.

2. How will you prepare benzaldehyde in laboratory and on an industrial scale? Compare and contrast its properties with those of acetaldehyde.

3. How will you prepare benzaldehyde from (a) toluene (b) benzene (c) benzal chloride and (d) benzonitrile.

How does benzaldehyde react with (a) dilute nitric acid (b) dilute potassium hydroxide (c) dry chlorine (d) sodium acetate and acetic anhydride (e) an excess of alkali.

4. Write short notes on :

(i) Cannizzaro's reaction (ii) Benzoin condensation (iii) Perkin's reaction (iv) Claisen's condensation (v) Reimer-Tiemann's reaction (vi) Etard's reaction.

5. Give the preparation, properties and uses of (a) 'Hypnone' (b) Benzophenone and (c) Salicylaldehyde.

6. Give the preparation and five different properties (naming the resultants) and one use of acetophenone. (Panjab Inter 1960)

7. (a) How is diphenyl ketone prepared? (Panjab Inter 1960)

(b) Present a scheme to obtain cinnamic acid from benzaldehyde. (Panjab Inter 1959 S)

8. Describe the reactions which are characteristic of benzaldehyde but are not given by acetaldehyde. (Panjab Inter 1957 S)

9. For what purpose are the following employed in aromatic chemistry : (a) Cannizzaro's reaction (b) Friedel-Craft's reaction (c) Etard's reaction (d) Perkin's reaction (e) Reimer-Tiemann's reaction (f) Kolbe's reaction (g) Benzoin condensation (h) Claisen's condensation. (Panjab Inter 1959 S)

10. Give the preparation, outstanding reactions and uses (if any) of benzaldehyde. How would you distinguish it from acetaldehyde? (Panjab Inter 1952 S)

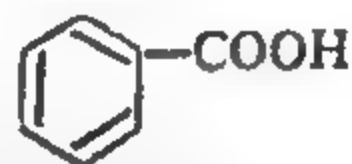
11. Describe how Etard's reaction is carried out with toluene. State at least five important properties of the product of this reaction. (Panjab Inter 1951)

CHAPTER LIII

AROMATIC CARBOXYLIC ACIDS

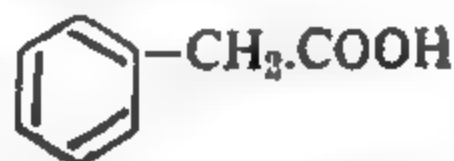
Aromatic carboxylic acids are compounds derived from the aromatic hydrocarbons by replacement of one or more than one hydrogen atoms by the carboxylic ($-\text{COOH}$) groups. These are of two types:

(i) Those in which the *carboxyl group is directly linked to the benzene nucleus*, for example, benzoic acid.



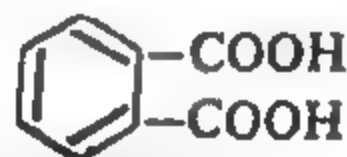
Benzoic acid

(ii) Those in which the *carboxyl group is present in the side chain*, for example, phenyl acetic acid.



Phenyl acetic acid

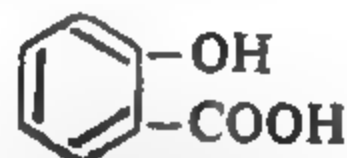
Acids are termed as mono, di- or tri-carboxylic acids if one, two or three hydrogen atoms respectively are replaced by $-\text{COOH}$ groups.



Phthalic acid

Phthalic acid is an important dicarboxylic acid.

Hydroxy substituted acids are also known, for example, salicylic acid.



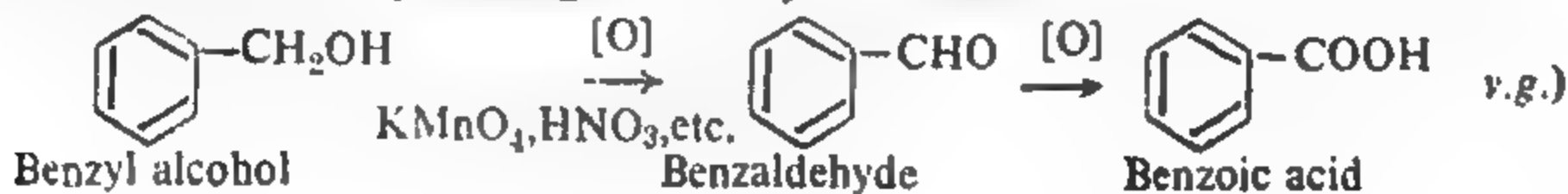
Salicylic acid
(*o*-Hydroxy benzoic acid)

BENZOIC ACID, $\text{C}_6\text{H}_5\text{COOH}$

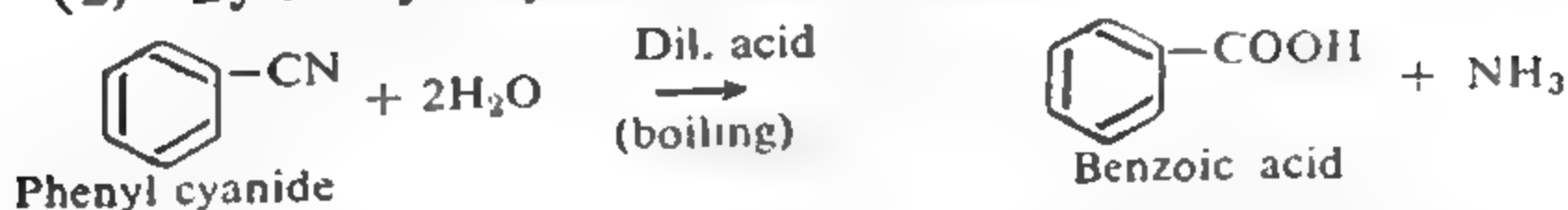
Benzoic acid occurs naturally in gum-benzoin (*luban*) and various other resins. It is also present in horse's urine as hippuric acid (benzoyl derivative of glycine, $\text{C}_6\text{H}_5\text{CO.NH.CH}_2\text{COOH}$).

Preparation. Benzoic acid may be prepared by the following methods :

(1) **By the oxidation of benzyl alcohol or benzaldehyde.** Benzyl alcohol or benzaldehyde may be oxidised by dilute nitric acid or chromic acid or alkaline potassium permanganate to yield benzoic acid.

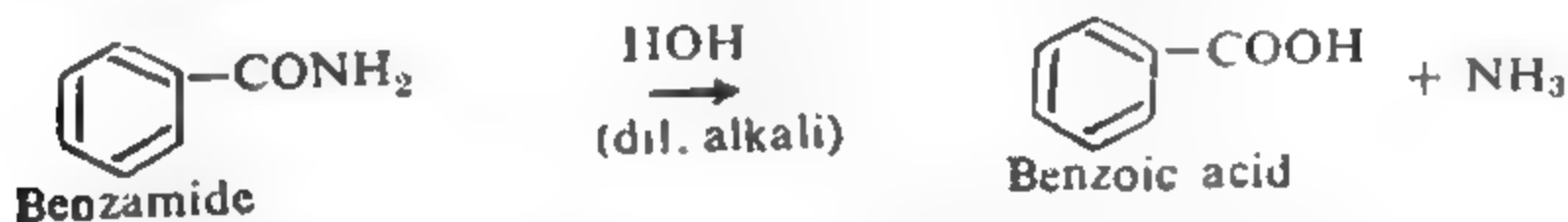
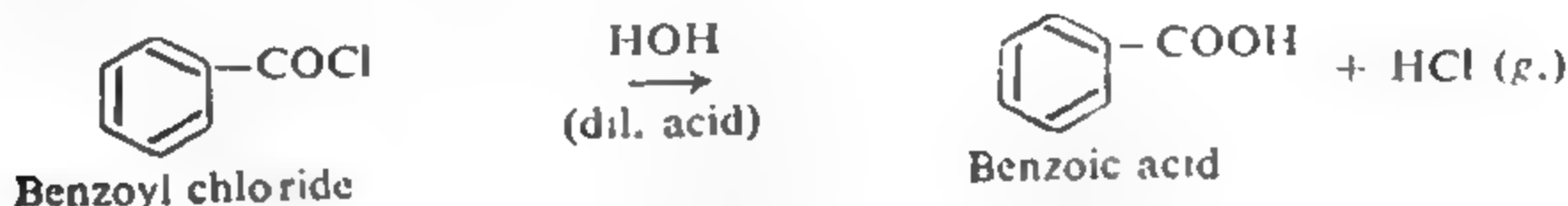


(2) By the hydrolysis of phenyl cyanide.



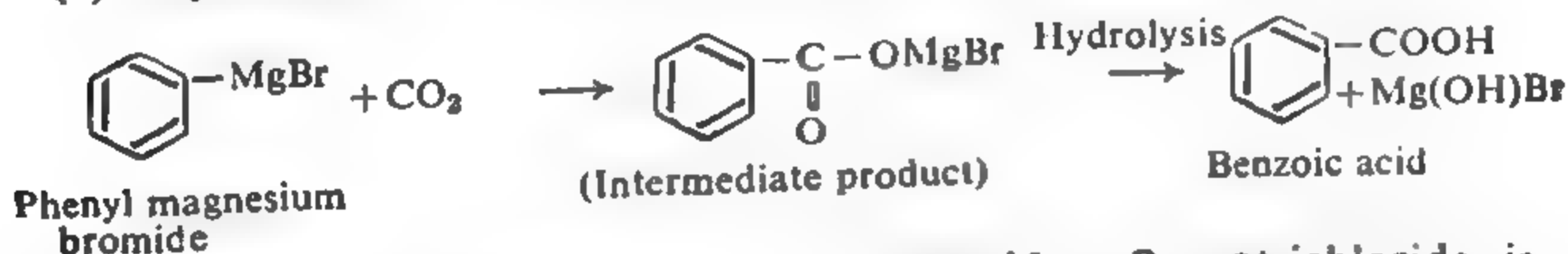
It may be recollected that phenyl cyanide may be obtained from benzene (a) through sulphonation or (b) through diazonium salt.

(3) By the hydrolysis of benzoyl chloride or benzamide. Benzoyl chloride or benzamide may be hydrolysed by boiling with dilute acid or dilute alkali, to yield the acid.

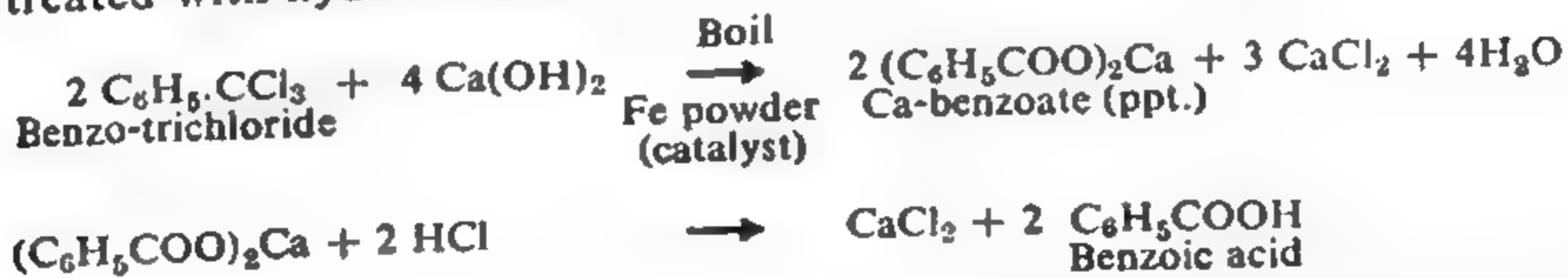


Benzoic acid is industrially obtained from benzoyl chloride which is obtained from benzene through Friedel and Craft reaction.

(4) By means of the corresponding Grignard reagent. (v.g.)

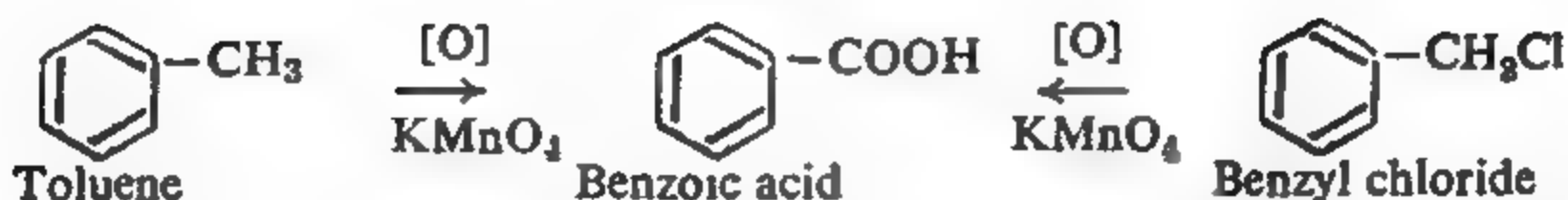


(5) By the hydrolysis of benzotrichloride. Benzotrichloride is hydrolysed by boiling with milk of lime containing a little iron powder (catalyst). Benzoic acid formed reacts with the excess of calcium hydroxide to give a precipitate of calcium benzoate. This is separated by filtration and treated with hydrochloric acid to regenerate benzoic acid.

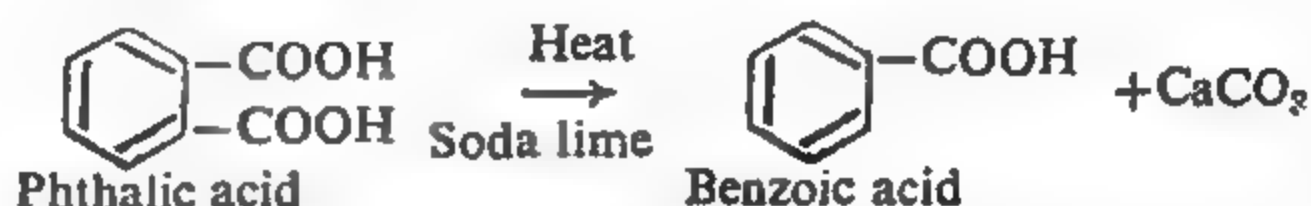


This method is industrially employed for the manufacture of benzoic acid. Toluene (from coal tar) is fully chlorinated to yield benzotrichloride which is treated as above.

(6) By the oxidation of a homologue of benzene or a derivative of benzene carrying a side chain. Toluene or benzyl chloride can be oxidised with dilute nitric acid or alkaline potassium permanganate to yield benzoic acid.



(7) By decarboxylation of phthalic acid. Phthalic acid on heating with lime or soda-lime, forms benzoic acid.



This method is very widely employed for commercial preparation of benzoic acid because phthalic acid is quite easily obtained by oxidation of naphthalene, occurring in coal tar.

Laboratory Preparation. Benzoic acid is conveniently prepared by the oxidation of benzyl chloride with alkaline potassium permanganate.

5 gm. of benzyl chloride and sodium carbonate solution (obtained by dissolving 5 gm. in 50 c.c. of water) are refluxed for about two hours. During this interval about 150 c.c. of 8% potassium permanganate solution are added, in small instalments through the condenser (Fig. 1). At the end, the precipitated manganese dioxide (from the potassium permanganate) is dissolved by passing sulphur dioxide through the reaction mixture. On cooling, dirty white crystals of benzoic acid are thrown down, which are filtered, washed and purified by recrystallisation from hot water.

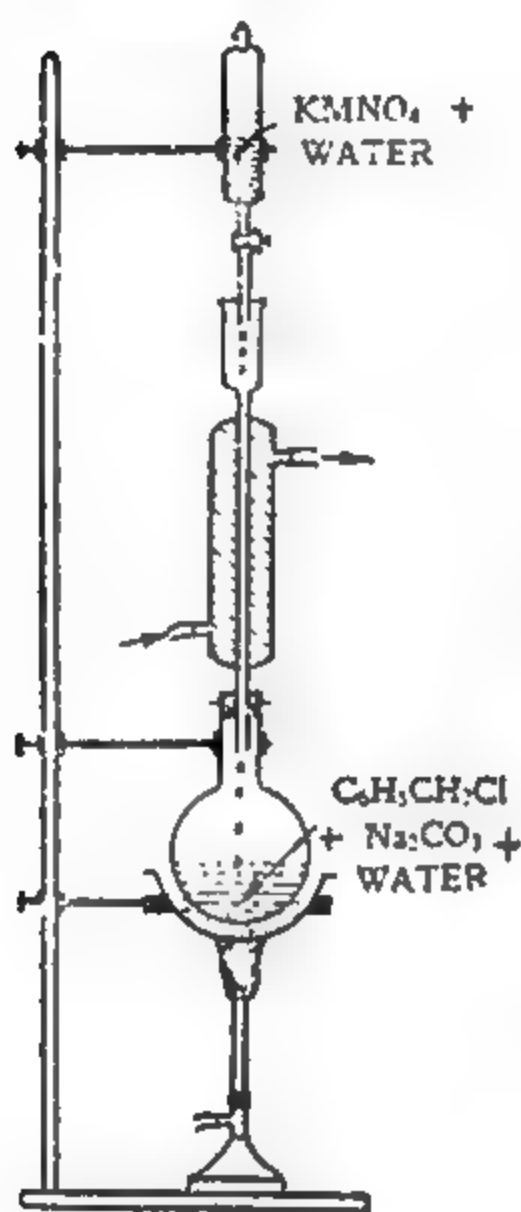


Fig. 1. Preparation of benzoic acid.

Physical Properties. Benzoic acid is a shining white crystalline solid (m.p. 121.5° , b.p. 249°) soluble in hot water, but sparingly soluble in cold water. It is soluble in alcohol, ether and benzene. It is volatile in steam and sublimes on rapid heating. Its vapour are very irritating and cause coughing and sneezing.

Chemical Properties. Chemically, benzoic acid shows the characteristic properties of the carboxyl group and those of the benzene nucleus. As such, the properties may be studied under the following heads ;

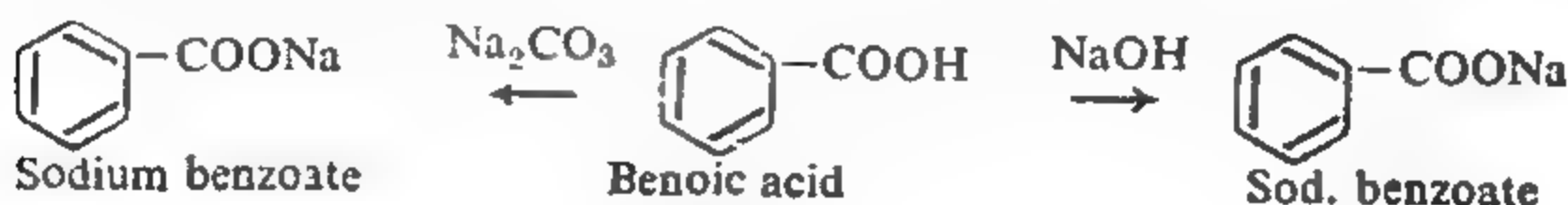
(a) Reactions of $-\text{COOH}$ Group.

(b) Reactions of Benzene Nucleus.

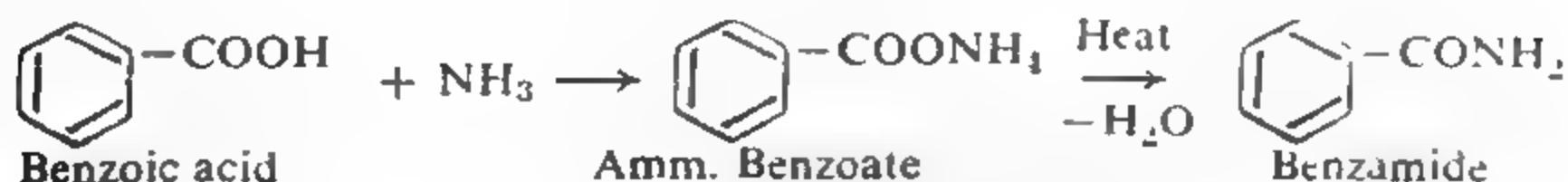
(a) Reactions of $-\text{COOH}$ Group

Benzoic acid is a stronger acid than acetic acid. It shows the usual properties of the H^+ ion.

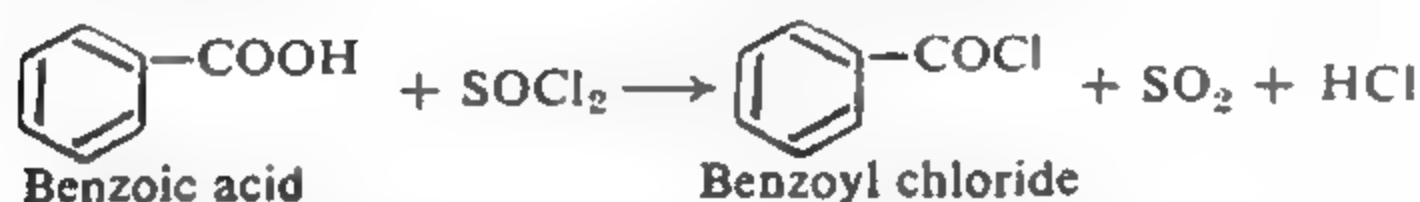
(1) Reaction with alkalis. It reacts with alkalis or carbonates to form the corresponding salts.



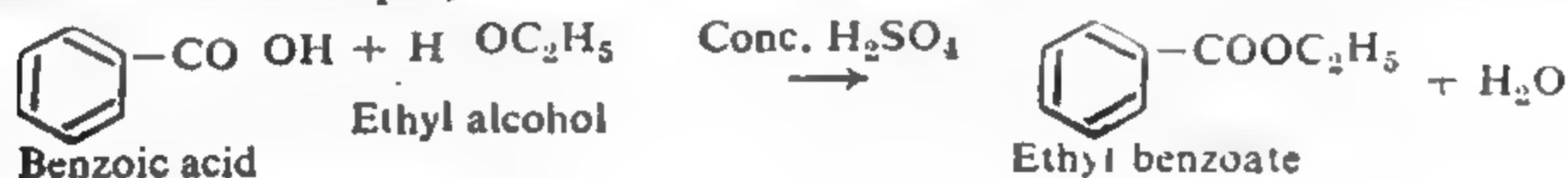
With ammonia, it forms the ammonium salt which on heating yields benzamide.



2. **Reaction with phosphorus pentachloride and thionyl chloride.** It reacts with phosphorus pentachloride or thionyl chloride to yield benzoyl chloride.



3. **Reaction with alcohols.** With alcohols, it forms the corresponding esters. For example,



4. **Decarboxylation with soda lime.** (i) The sodium salt of benzoic acid when heated with soda lime yields benzene.



5. **Reactions of salts.** (i) The calcium salt on dry distillation yields benzophenone.



(ii) The calcium salt, when distilled with calcium formate, yields benzaldehyde.

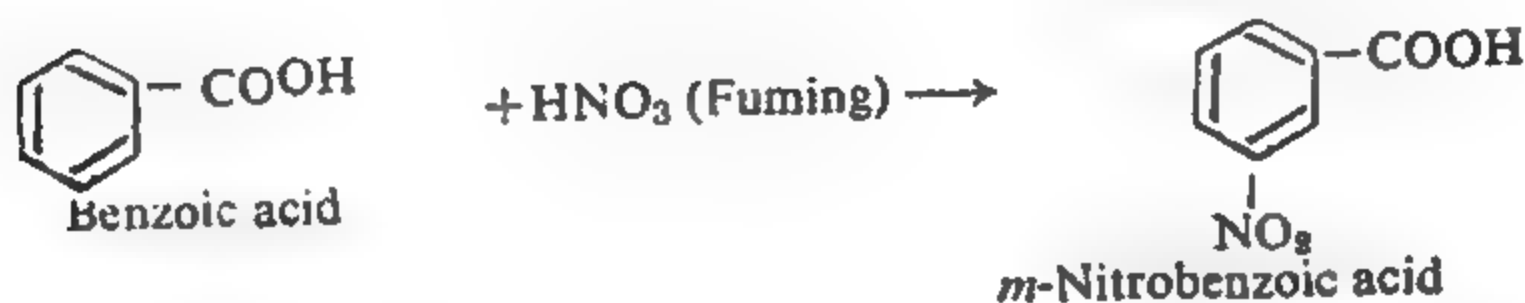
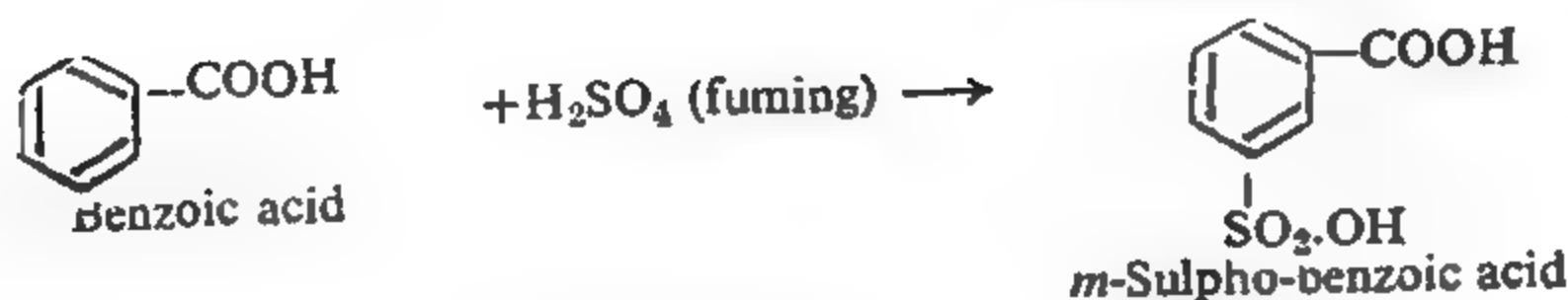


(iii) The sodium salt when distilled with benzoyl chloride forms benzoic anhydride.



(b) Reactions of Benzene Nucleus

Benzoic acid shows the usual reactions of the benzene nucleus. It undergoes halogenation, nitration and sulphonation, yielding meta derivatives.



Uses. Benzoic acid is used : (i) in medicine as a urinary antiseptic and for disinfecting bronchial tubes (ii) as a fruit preservative in the form of its sodium salt (iii) in the manufacture of dyestuffs.

Tests. (1) Benzoic acid is insoluble in cold water, but dissolves in hot water.

(2) When sodium bicarbonate is added to an aqueous solution of benzoic acid, carbon dioxide is evolved.

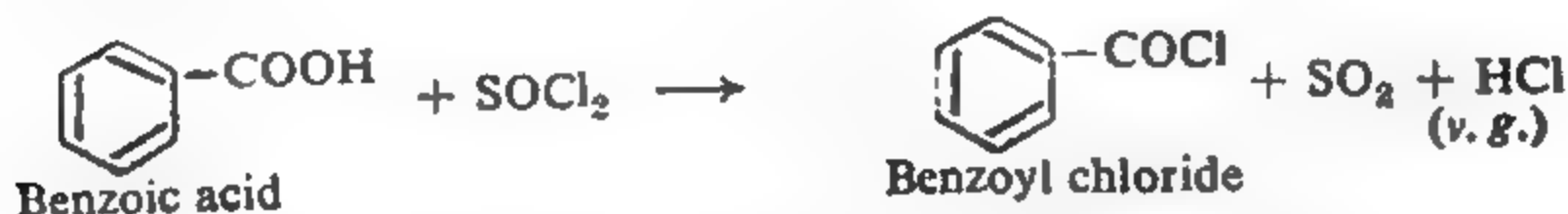
(3) Benzoic acid, on distillation with soda lime, yields inflammable vapour of benzene.

(4) If ferric chloride is added to a neutral solution of benzoic acid, a buff coloured precipitate is obtained.

Benzoyl Chloride, $\text{C}_6\text{H}_5\text{COCl}$

Benzoyl chloride is obtained by the following methods :

(i) By distilling benzoic acid with phosphorus pentachloride or thionyl chloride.



(ii) By passing chlorine through boiling benzaldehyde.



Industrially, benzoyl chloride is prepared by this method.

(iii) It is also obtained by Friedel and Craft's reaction by the interaction of benzene with carbonyl chloride in the presence of anhydrous aluminium chloride.



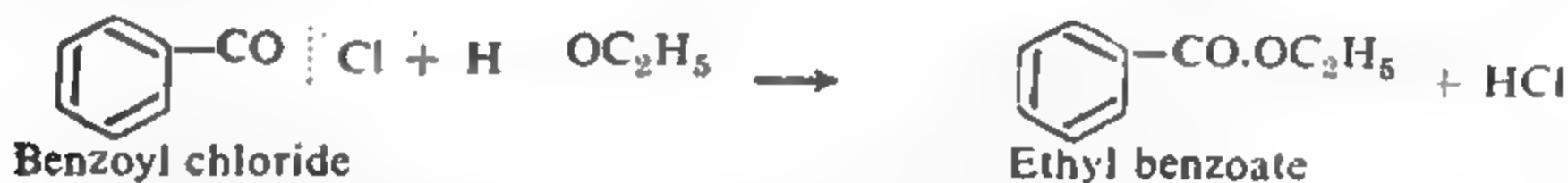
Physical Properties. Benzoyl chloride is a colourless liquid (b.p. 197°) with a strong pungent odour. It fumes in air. Its vapours bring tears in eyes and attack mucous membrane of the nose.

Chemical properties. Chemically, it resembles acetyl chloride.

1. **Hydrolysis.** It is slowly hydrolysed with water but rapidly with dilute alkalis, to yield benzoic acid.



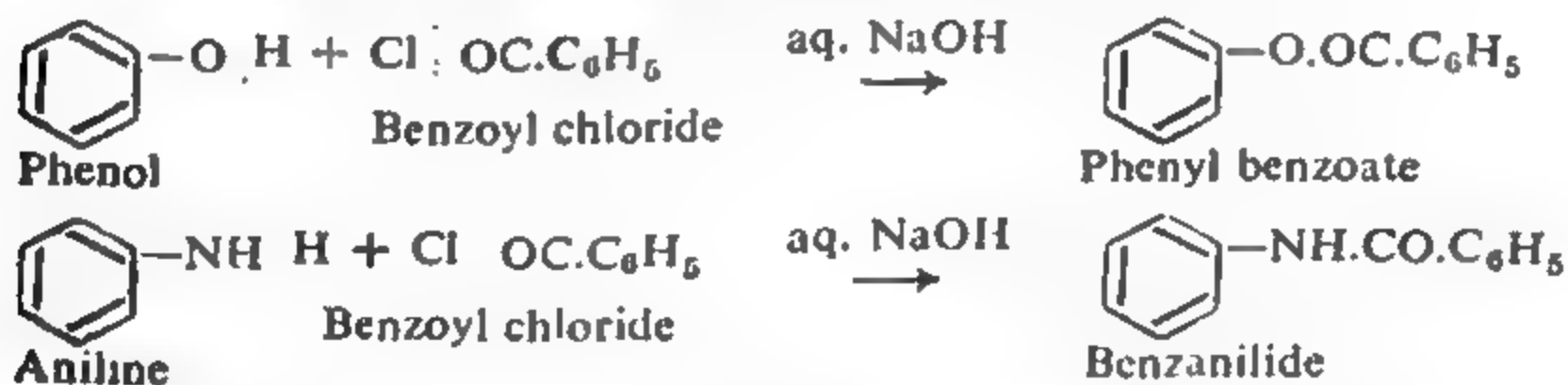
2. **Reaction with alcohol.** It reacts with ethyl alcohol to form ethyl benzoate.



3. **Reaction with ammonia.** Benzoyl chloride reacts with a concentrated solution of ammonia to form benzamide.



4. **Benzoylation.** Benzoyl chloride reacts with all compounds containing an amino group or a hydroxyl group in such a way that the hydrogen atom is replaced by the benzoyl ($\text{C}_6\text{H}_5\text{CO}-$) group. This reaction is carried out in the presence of aqueous alkali.

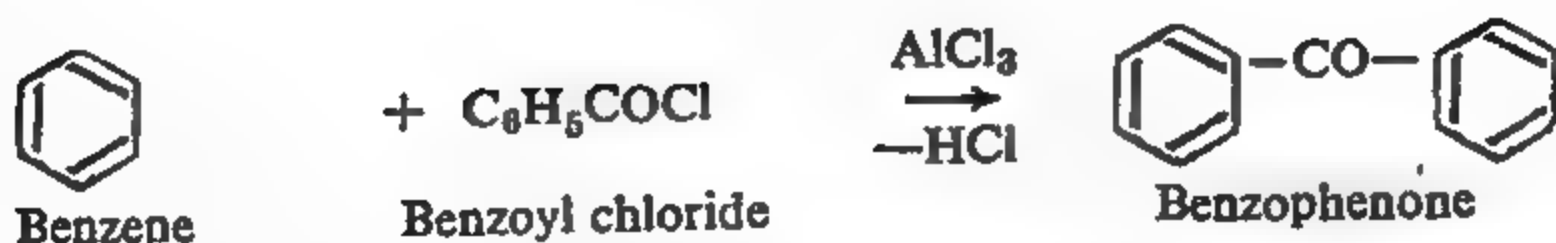


The replacement of an active hydrogen atom by a benzoyl group is known as **Schotten-Baumann's reaction**.

5. When distilled with anhydrous sodium benzoate, benzoic anhydride is formed.



6. When treated with benzene in the presence of anhydrous aluminium chloride, it gives benzophenone (Friedel-Craft's reaction).

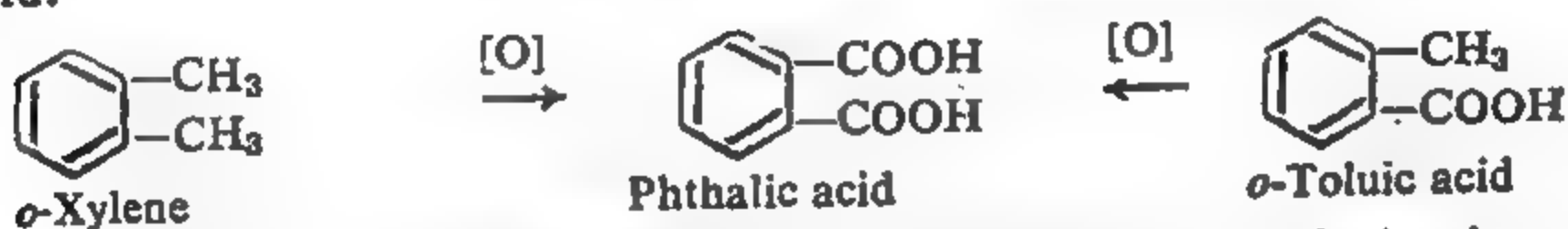


Uses. Benzoyl chloride is used for benzylation purposes.

PHTHALIC ACID, $\text{C}_6\text{H}_4(\text{COOH})_2$

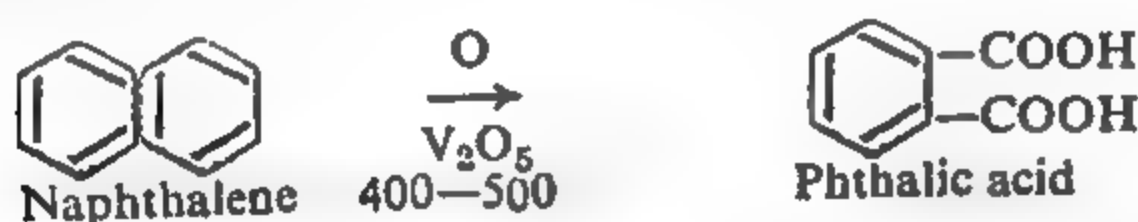
Ortho-phthalic acid or simply phthalic acid is a typical and the most important of the benzene dicarboxylic acids.

Preparation. (1) By the oxidation of *o*-xylene. Ortho xylene (or *o*-toluic acid) on oxidation with alkaline potassium permanganate yields phthalic acid.



In fact, it may be obtained by the oxidation of any derivative of benzene containing two side chains in 1 : 2 positions.

(2) On an industrial scale, it is obtained by the oxidation of naphthalene by passing its vapours mixed with air over vanadium pentoxide heated to 400—500°.

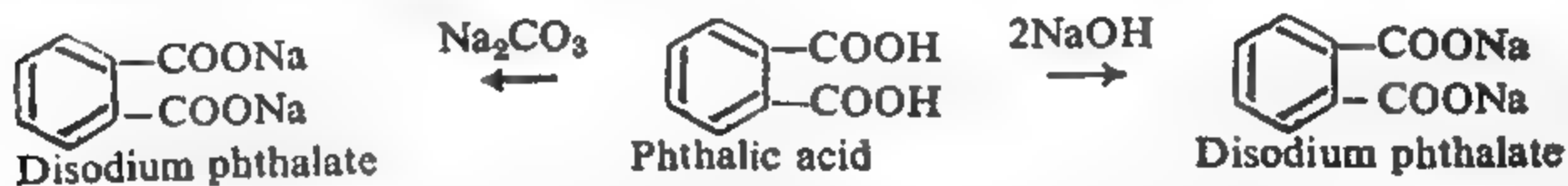


In actual practice phthalic anhydride is obtained first, which on boiling with water is converted into phthalic acid.

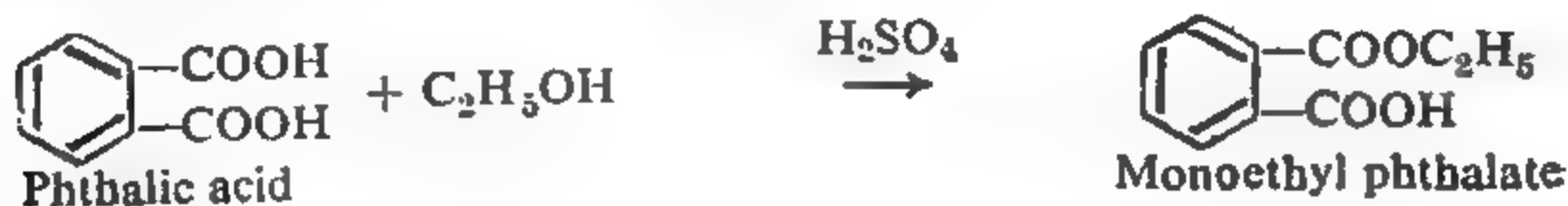
Physical Properties. Phthalic acid is a white crystalline solid. It melts at 231°, when a part of it is converted into its anhydride. It is sparingly soluble in cold water but dissolves in hot water.

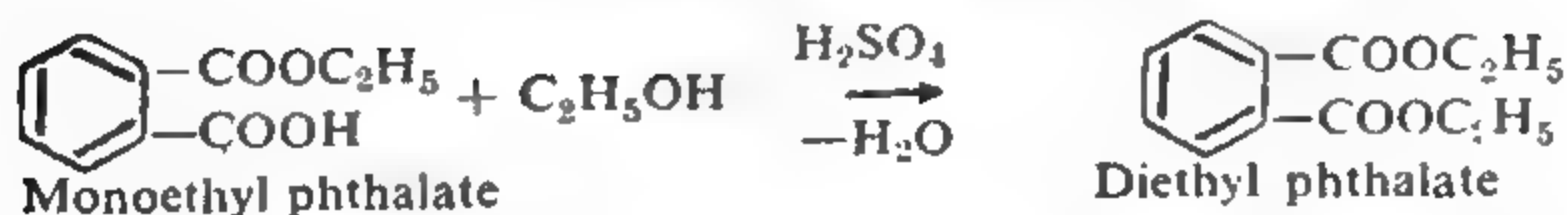
Chemical Properties. Chemically, it shows the typical properties of a dicarboxylic acid.

1. **Salt formation.** It reacts with alkalies and carbonates to yield corresponding salts.

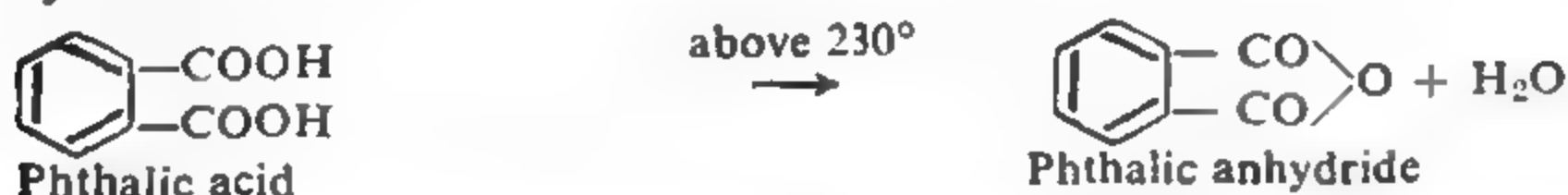


2. **Esterification.** It reacts with alcohols in the presence of concentrated sulphuric acid to yield the esters.





3. **Action of heat.** When heated above 230° , it forms phthalic anhydride.



4. **Reaction with phosphorus pentachloride.** With phosphorus pentachloride, phthalic acid yields phthalyl chloride.



5. **Distillation with lime.** When phthalic acid is distilled with lime, benzoic acid is formed.



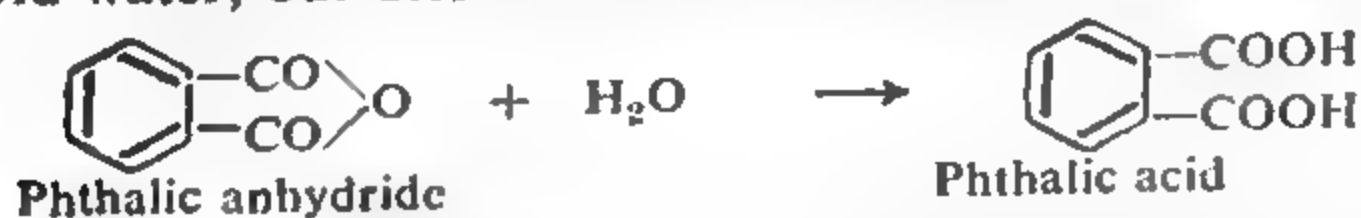
Uses. Phthalic acid is used in the manufacture of phthalic anhydride, plasticizers and plastics. It is also used in the manufacture of dyestuffs such as eosin, fluorescein, etc.



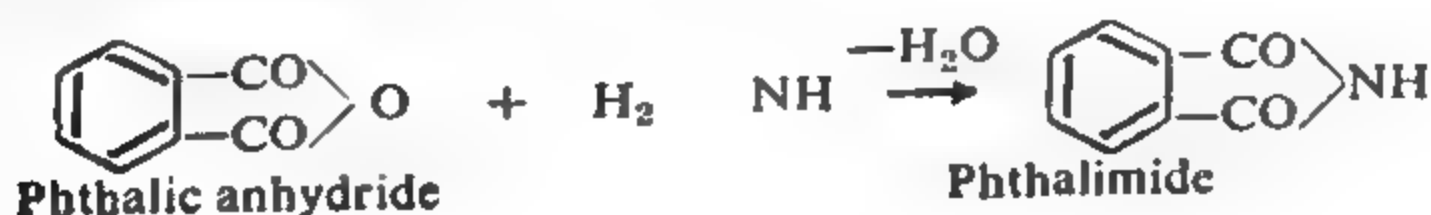
Phthalic anhydride is obtained by passing vapours of naphthalene and air over heated ($400-500^\circ$) vanadium pentoxide (catalyst).



Properties. It forms white needles (m.p. 128°). It is insoluble in cold water, but dissolves in hot water forming phthalic acid.



(2) When heated with dry ammonia at 200° under pressure, phthalimide is formed.

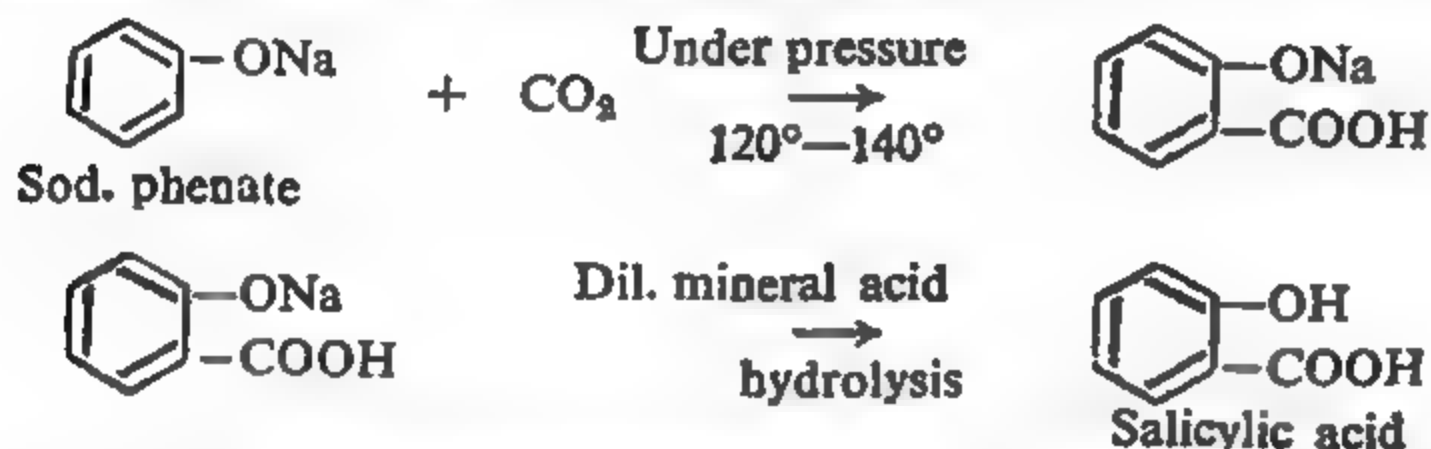


(3) When heated with a little phenol and a few drops of concentrated sulphuric acid, phthalic anhydride yields phenolphthalein (see properties of phenol).

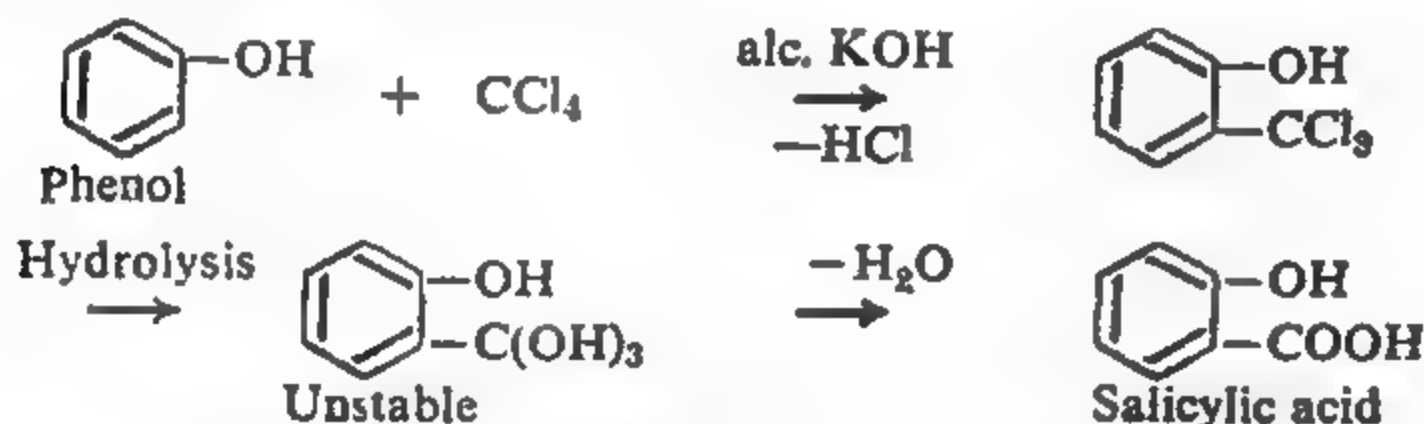
Salicylic Acid, *O*-Hydroxybenzoic acid, $C_6H_4(OH)COOH$

Salicylic acid occurs naturally as its methyl ester (*i.e.*, methyl salicylate) in oil of wintergreen.

Preparation. 1. By heating sodium phenate with carbon dioxide under pressure at $120-140^\circ$ (Kolbe's reaction).



2. By heating phenol with carbon tetrachloride and alcoholic caustic potash. (Reimer Tiemann's reaction). Phenol, mixed with an equimolecular proportion of carbon tetrachloride, is refluxed in the presence of alcoholic potash for 8 hours.

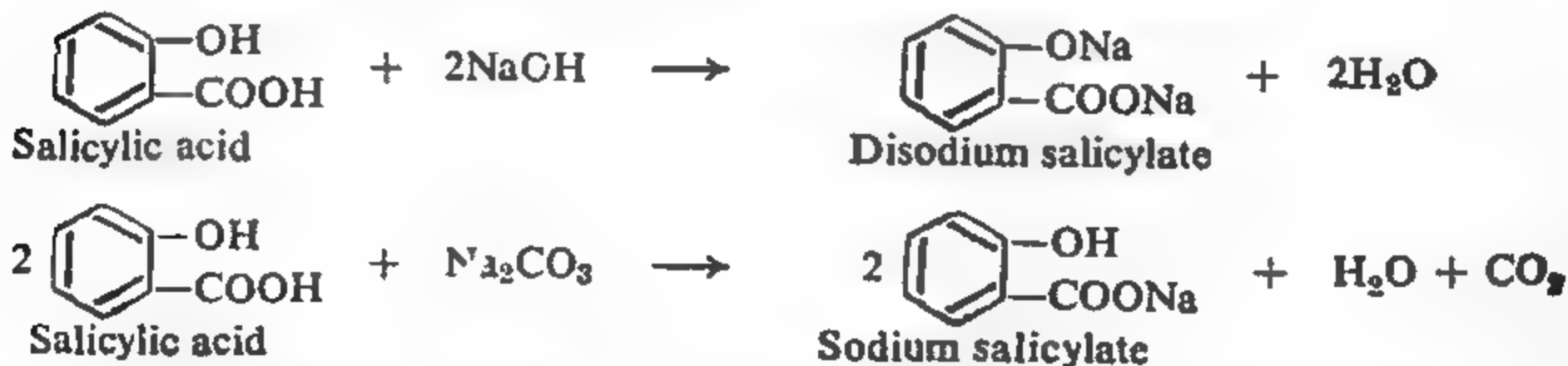


Physical Properties. Salicylic acid forms colourless needle-like crystals, melting at 159° . It is only sparingly soluble in cold water, but dissolves readily in hot water, alcohol and ether. It sublimes at 75° .

Chemical Properties. As expected from its structure, salicylic acid shows reactions characteristic of (i) *carboxyl group* (ii) *phenolic group* and (iii) *benzene nucleus*.

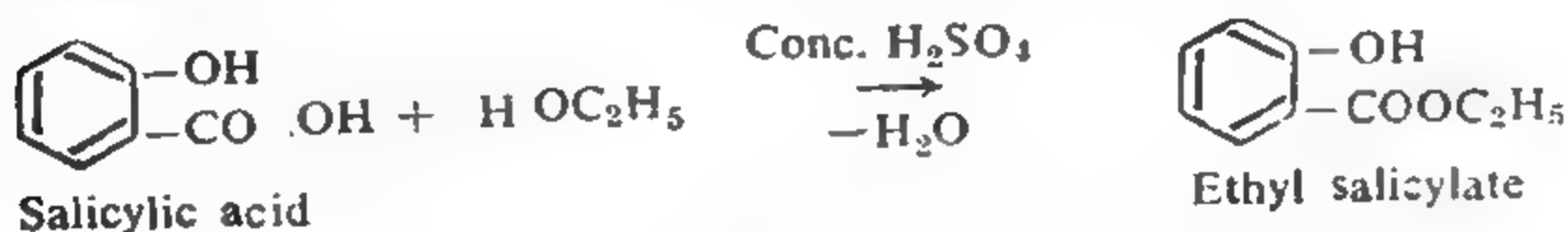
(i) Reactions of the Carboxyl Group

(1) It reacts with alkalies and carbonates to form salts.



Sodium carbonate does not attack the phenolic group.

(2) It reacts with alcohols in the presence of a suitable dehydrating reagent to give esters.



(3) When distilled with lime, it yields phenol.



(ii) Reactions of the Phenolic Group.

(1) It reacts with phosphorus pentachloride, acetyl chloride and zinc dust in the same manner as phenol does.



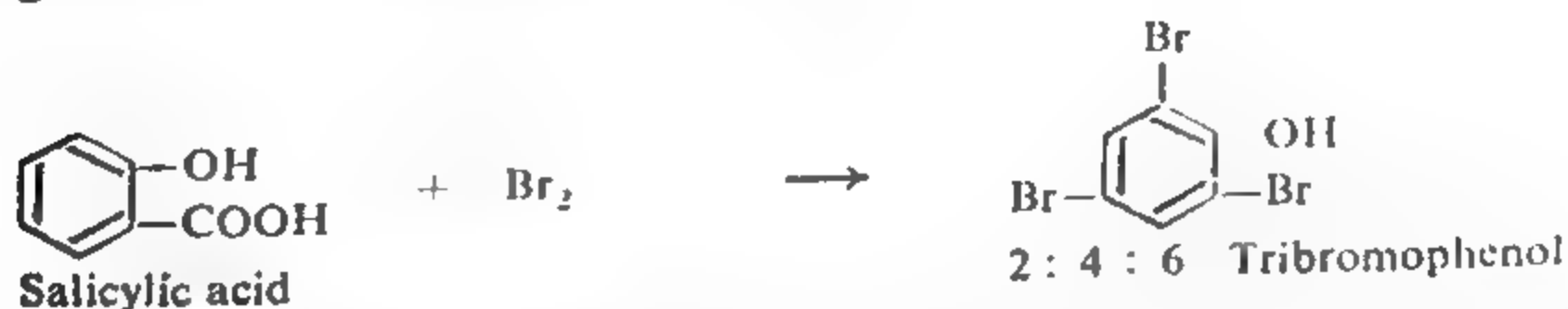
Phosphorus pentachloride attacks both the groups, viz., $-\text{OH}$ and $-\text{COOH}$ groups.



(2) With ferric chloride, salicylic acid gives a violet coloration.

(iii) Reactions of Benzene Nucleus

It shows the usual reactions of benzene nucleus. It can be halogenated, sulphonated and nitrated. For instance, with bromine water it gives 2 : 4 : 6 tribromo phenol.



Similarly, with fuming nitric acid, 2 : 4 : 6 trinitrophenol is obtained.

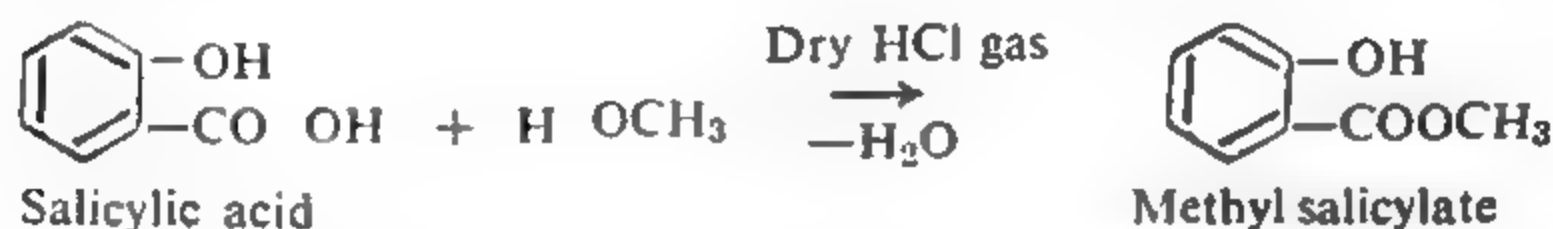
Uses. Salicylic acid is widely used (i) in medicine as an antiseptic

and for relieving rheumatic pains (ii) in the preparation of important compounds like aspirin, salol and methyl salicylate (iii) in the manufacture of azo-dyes.

Methyl Salicylate, $C_6H_4(OH)COOCH_3$

Methyl salicylate occurs naturally in oil of wintergreen.

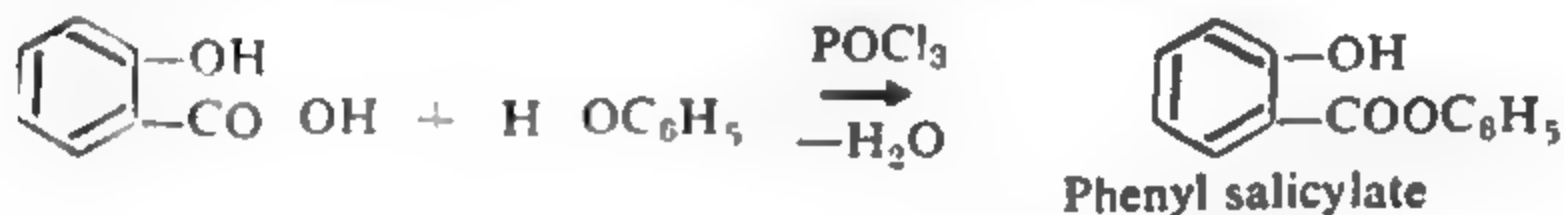
It is prepared by distilling salicylic acid and methanol in the presence of a suitable dehydrating reagent like concentrated sulphuric acid or dry hydrogen chloride (gas).



It is a colourless pleasant smelling liquid (b.p. 224°). It is used in perfumery and medicine as a specific treatment for aches, sprains and bruises.

Phenyl Salicylate or Salol, $C_6H_4(OH).COOC_6H_5$

Phenyl salicylate is obtained by heating salicylic acid, phenol and phosphorus oxychloride.



It is a white solid (m.p. 42°), almost insoluble in water. It is commonly used in medicine as an internal antiseptic.

Acetyl salicylic acid or Aspirin, $C_6H_4(O.COCH_3)COOH$

Acetyl salicylic acid or aspirin is prepared by acetylation of salicylic acid with acetyl chloride or acetic anhydride.

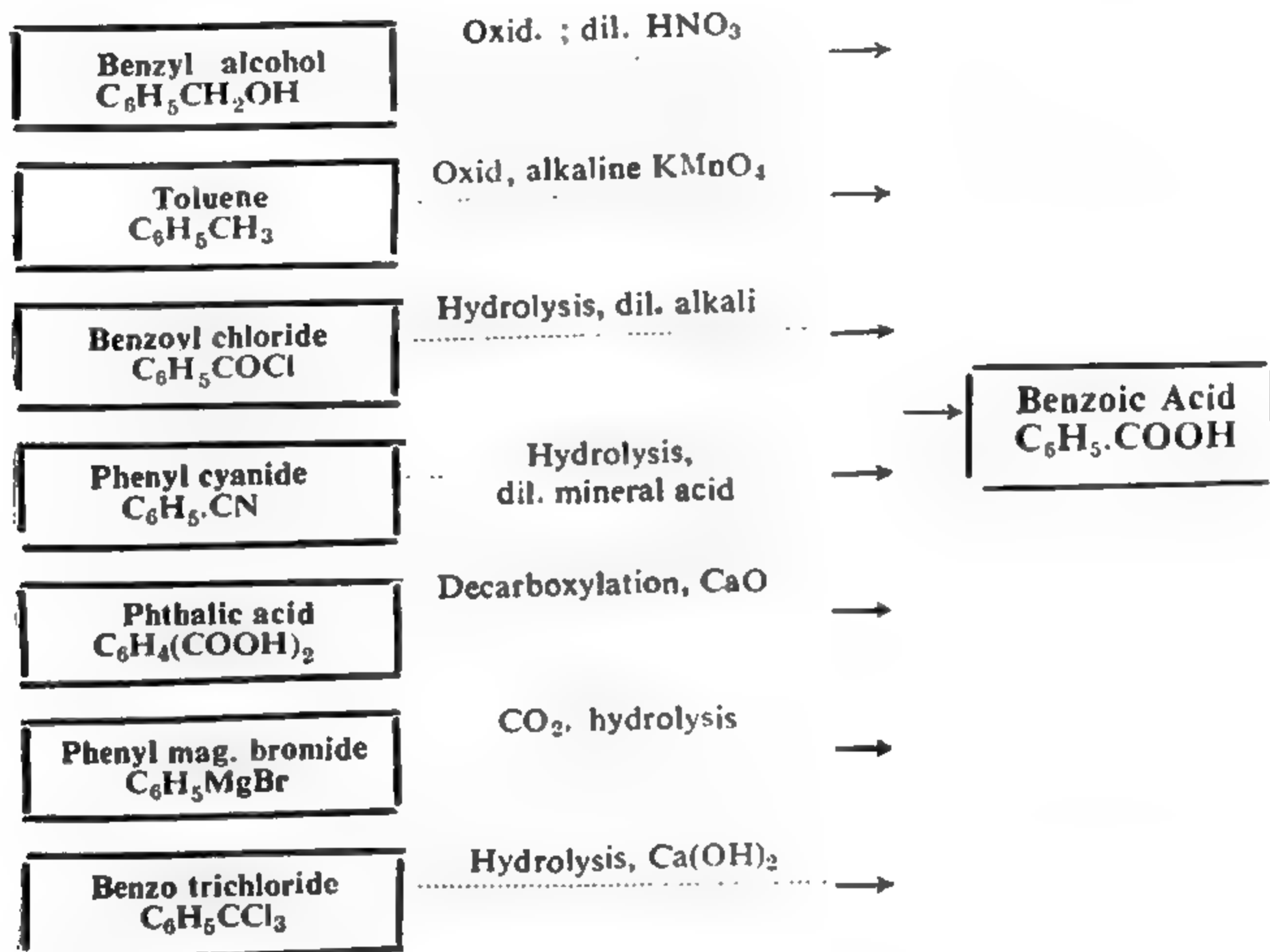


Aspirin is a white crystalline solid (m.p. 136°). It is sparingly soluble in cold water. It is extensively used in medicine for relieving pains (analgesic) and in fevers for lowering the temperature of the body (anti-pyretic). Large doses, however, are poisonous.

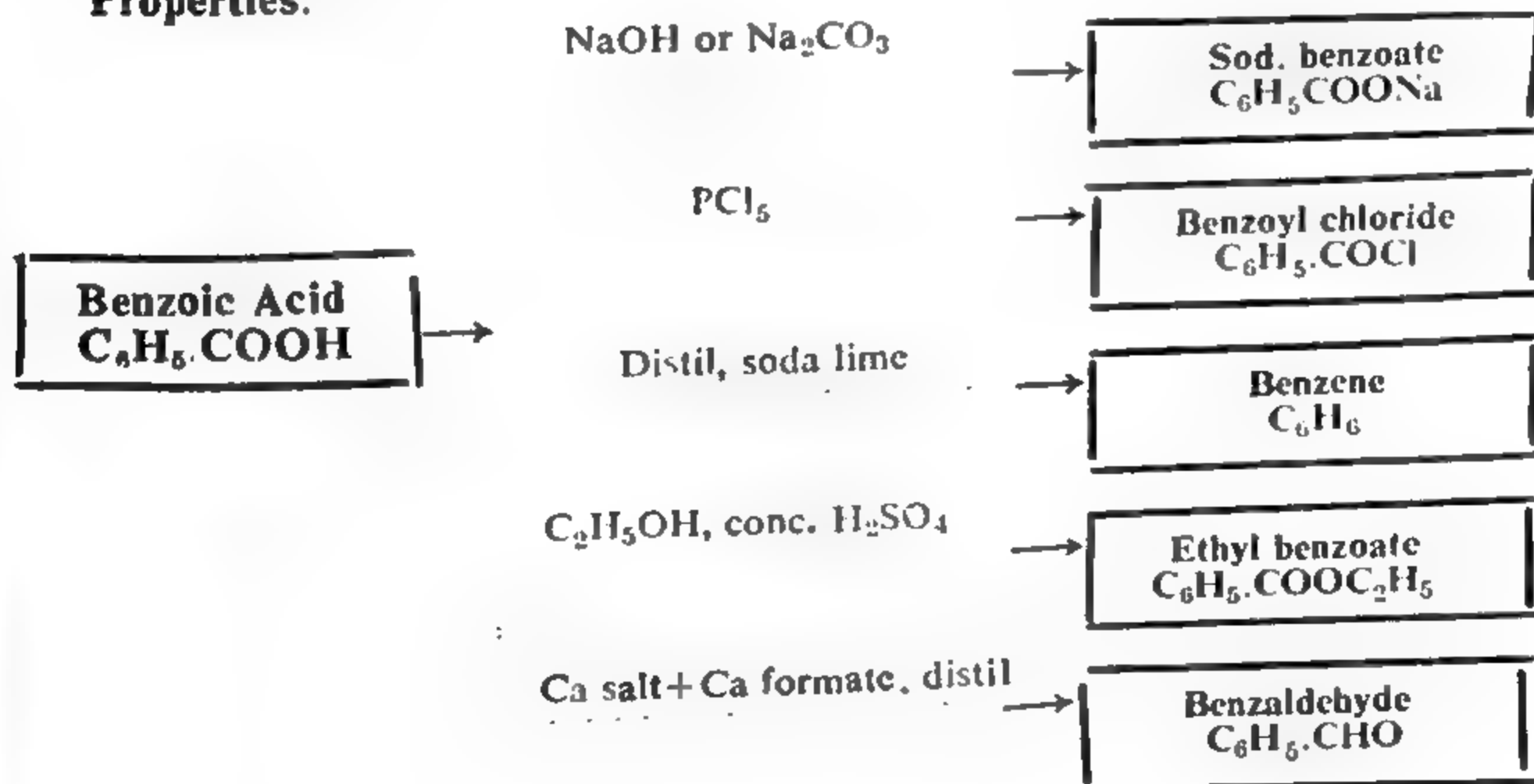
SUMMARY OF TYPICAL MEMBERS

PREPARATION AND PROPERTIES OF BENZOIC ACID

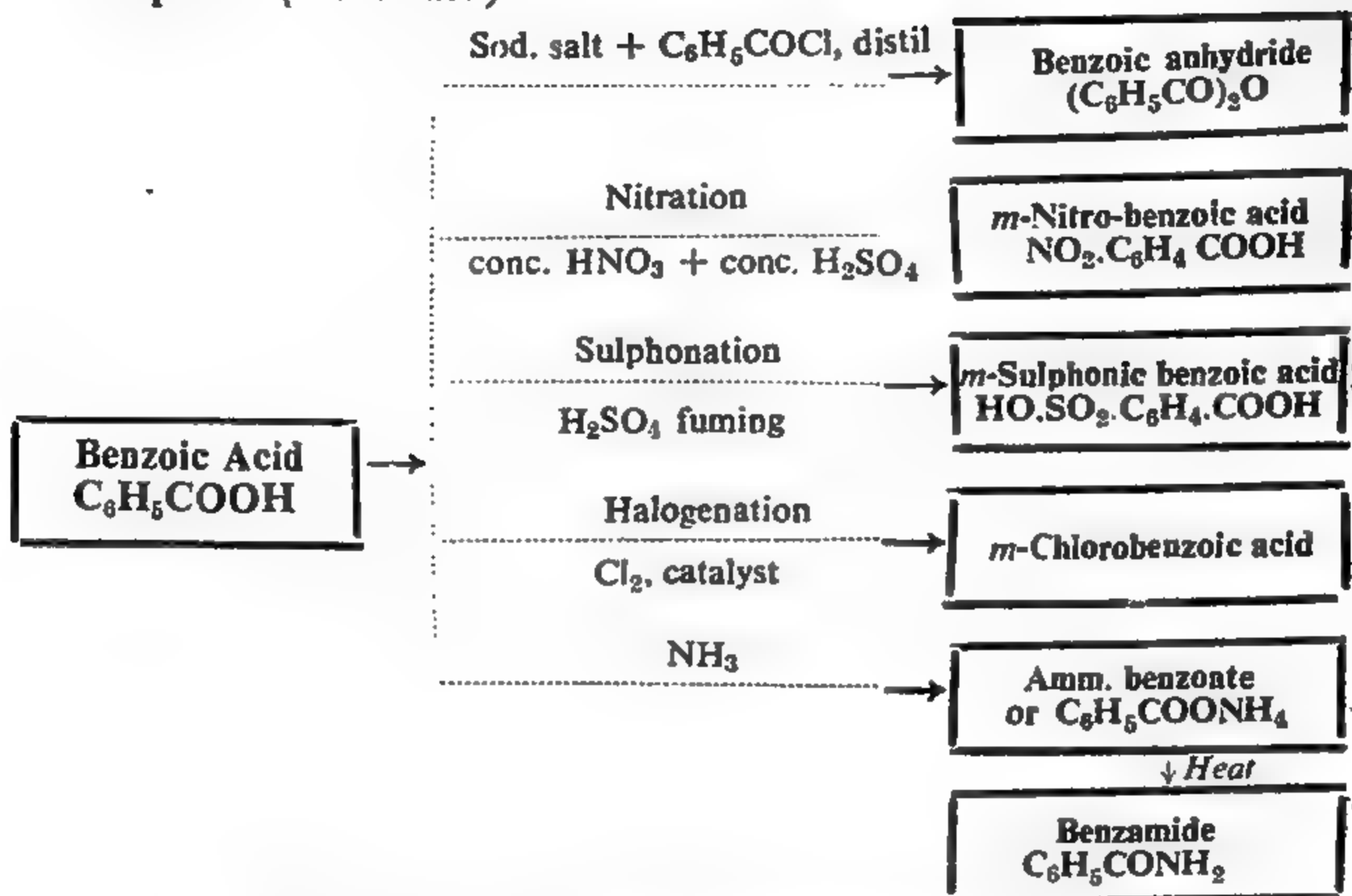
Preparation.



Properties.

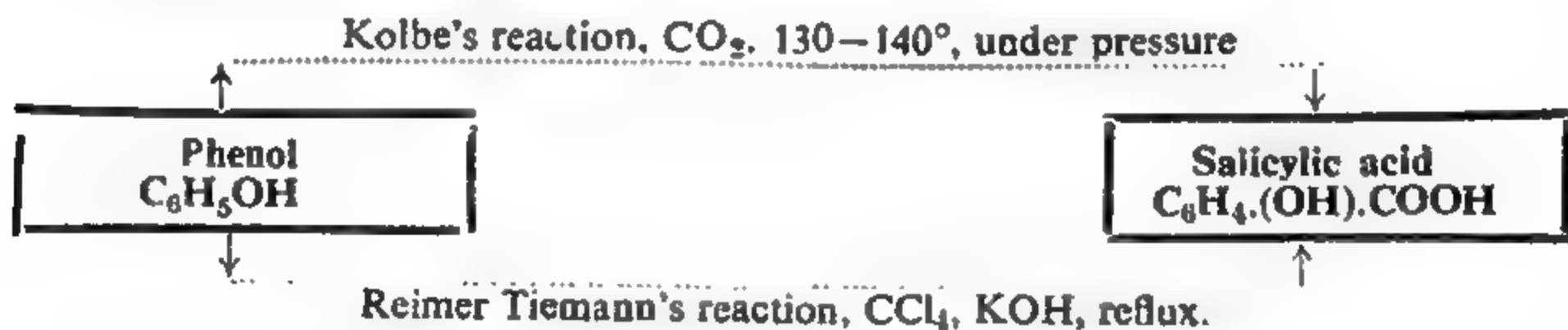


Properties (Continued)

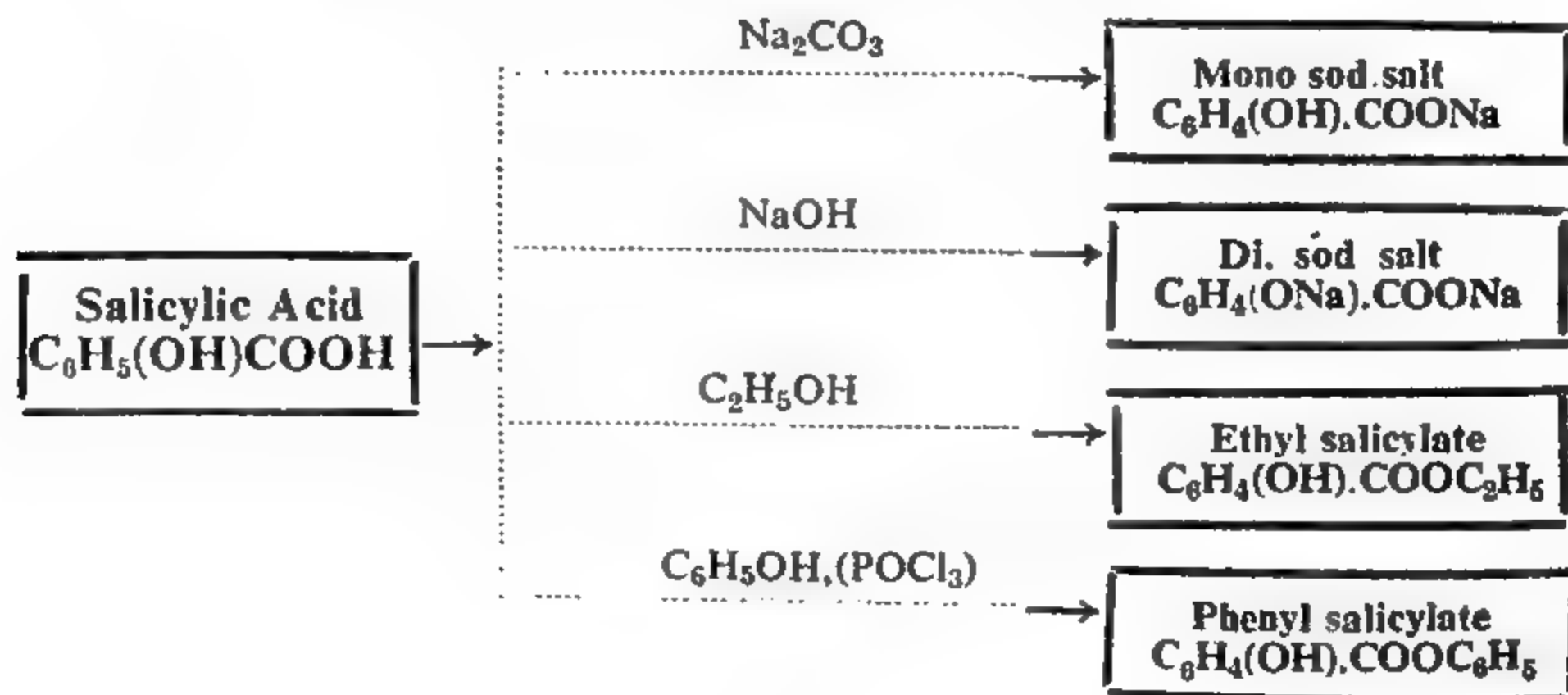


PREPARATION AND PROPERTIES OF SALICYLIC ACID

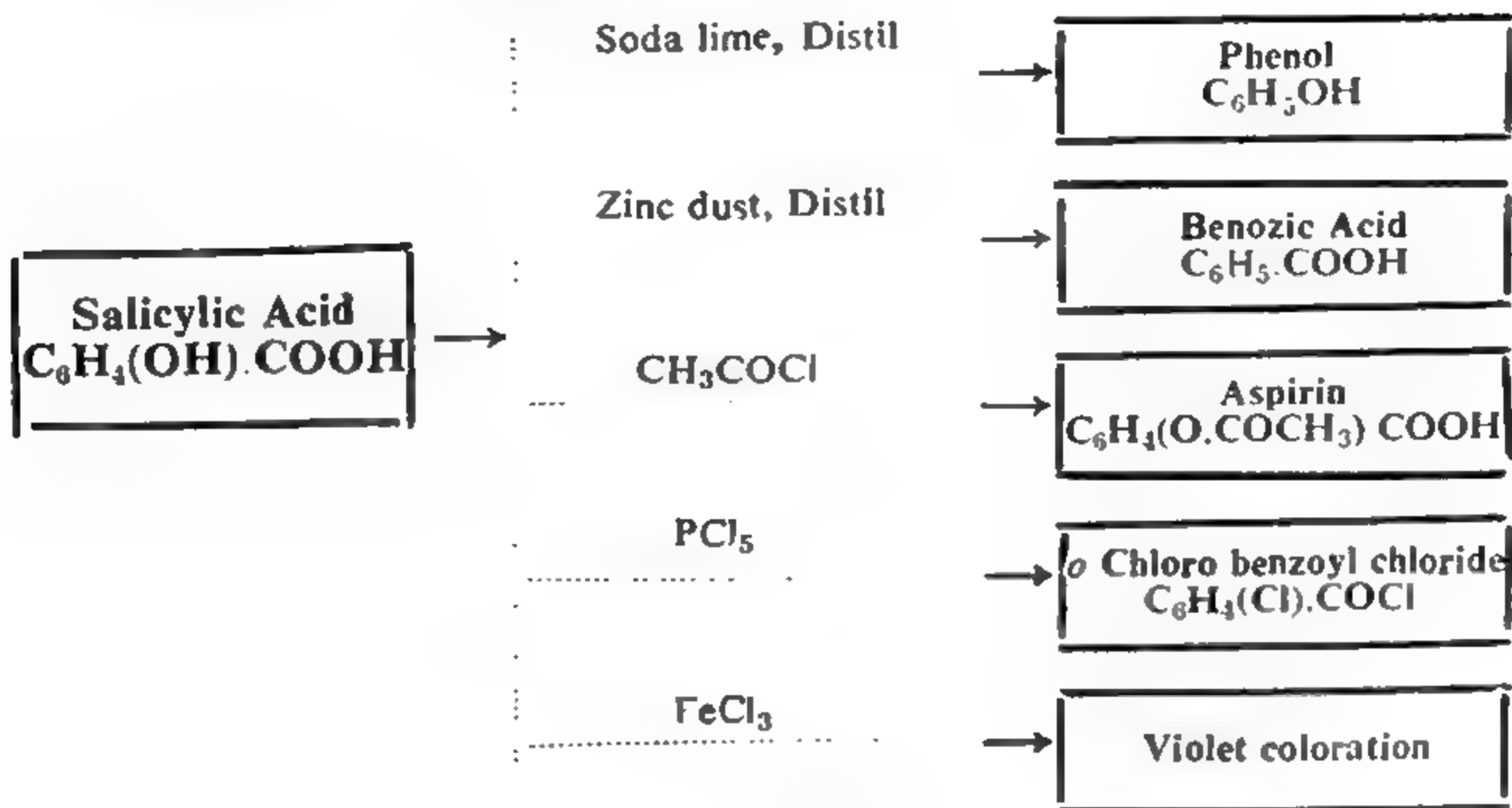
Preparation.



Properties.



Properties (Continued)



QUESTIONS

- What are aromatic acids? How do you differentiate them from aliphatic acids? Illustrate your answer with examples.
- How will you prepare benzoic acid (a) in laboratory (b) industrially?
How does benzoic acid react with (a) acetyl chloride (b) phosphorus pentachloride (c) bromine in the presence of halogen carrier.
- Give the preparation, properties and uses of benzoyl chloride.
- Represent schematically, how you would obtain benzoic acid from (a) phenol (b) benzoyl chloride (c) toluene and (d) aniline.
How does benzoic acid react with (a) hot soda lime (b) ammonium hydroxide and heating strongly and (c) heating alone?
- How will you obtain salicylic acid (a) in laboratory (b) industrially? How does salicylic acid react with (a) methyl alcohol (b) acetyl chloride (c) phenol? Name the compounds obtained in each case. What is their importance?
- Write short notes on :
(i) Aspirin (ii) Salol (iii) Benzoylation (iv) Phthalic anhydride.
- How is phthalic acid obtained on a large scale? Describe its properties. How does phthalic acid react with (a) phosphorus pentachloride (b) ethyl alcohol (c) ammonia (d) soda lime.
- How will you convert phenol, benzene sulphonic acid, phenyl nitrile, benzyl chloride and phthalic acid into benzoic acid? Give equations and the experimental conditions, where possible.
- State four methods of preparation of an aromatic acid and four properties of benzoic acid. (Panjab Inter 1961 S)
- Represent the steps by which (a) phenol (b) benzene can be converted into benzoic acid.
(b) Give the preparation, properties and uses of (a) acetanilide (b) phthalic acid. (Panjab Inter 1961, 1959)

11. Give the method of preparing phthalic anhydride. How does it react with (i) water (ii) ammonia (iii) phenol with a drop of conc. H_2SO_4 ? (*Panjab Inter 1951 S*)
12. How are the following compounds obtained from salicylic acid; (i) Phenol (ii) Aspirin (iii) Salol (iv) Methyl salicylate? (*Panjab Inter 1958 S*)
13. How does benzoyl chloride react with the following compounds; (a) ammonia (b) methyl alcohol (c) water (d) phenol (e) aniline? Give equations and name the important products in each reaction. (*Panjab Inter 1958 S*)
14. Describe (a) Kolbe's reaction (b) Reimer Tiemann's reaction for the preparation of salicylic acid. How are the following prepared from salicylic acid: (a) methyl salicylate (b) aspirin (c) salol? (*Panjab Inter 1957 S*)
15. Give the outlines of methods for the preparation of benzoic acid and indicate how far these are similar to the methods used in the preparation of fatty acids. Under what conditions (a) benzamide (b) benzoyl chloride is converted into benzoic acid? (*Panjab Inter 1957 S*)
16. Give the laboratory preparation of benzoic acid. Enumerate its important reactions and tests. (*Panjab Inter 1955 S*)
17. Give the preparation and reactions of aromatic dicarboxylic acids. Give the name and formula of an acid from the aliphatic series which can give similar reactions. (*Panjab Inter 1954*)

APPENDIX I

MISCELLANEOUS QUESTIONS

(A) Structural Formula.

1. Two organic substances *A* and *B* were found to contain carbon = 40.0 and hydrogen = 6.7 per cent ; the remainder being oxygen in both cases. The vapour density of *A* was 15, that of *B* was 30. *A* reduced Fehling solution, but did not effervesce with sodium carbonate ; *B* did not reduce Fehling solution but effervesced when added to sodium carbonate solution. Deduce the molecular and structural formulae of *A* and *B*.

[Ans. CH_2O , $\text{C}_2\text{H}_4\text{O}_2$; HCHO ; CH_3COOH] (*Jammu and Kashmir Inter 1953*)

2. (i) 0.2905 gm. of an organic monobasic acid when burnt yielded 0.6160 gm. of CO_2 and 0.0945 gm. of H_2O .

(ii) On heating with soda lime, its sodium salt gave benzene.

(iii) It forms two series of salts and two series of esters.

(iv) It furnishes an anhydride on simple heating.

From the above facts about the acid, find out its structural formula.

[Ans. $\text{C}_6\text{H}_4(\text{COOH})_2$, Phthalic acid] (*Panjab Inter 1951*)

3. A dicarboxylic acid was analysed as follows :

0.378 gm. on combustion give 0.264 gm. of carbon dioxide and 0.162 gm. of water vapour.

0.105 gm. in solution neutralised exactly 25 milli-litres of N.15 NaOH.

Assign a formula to the acid. [Ans. $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$] (*P. U. Inter 1952*)

4. A dibasic acid containing only C, H and O was found by analysis to contain C = 26.7% and H = 2.2%. The vapour density of its diethyl ester was found to be 73. What is the acid ?

[Ans. $(\text{COOH})_2$] (*Jammu and Kashmir Inter 1959*)

5. 15.0 c.c. of a gaseous hydrocarbon were exploded with 105.5 c.c. of oxygen. After cooling, the residual gas occupied 75.0 c.c. On treatment with a strong solution of caustic potash, the volume was further reduced to 30.0 c.c. Determine the molecular formula of the hydrocarbon, name it and write its structural formula.

[Ans. C_3H_8 , propane, $\text{CH}_3\text{CH}_2\text{CH}_3$] (*P.U. T.D.C. Part I Exam. 1962*)

6. Write down the structural formula of each member of the following parts of isomers :

(a) Normal and iso-butanes (b) Ethyl acetate and methyl propionate (c) Normal and iso-propyl groups (d) 1, 1-and 1, 2-dibromoethane. (*Aligarh Inter 1959*)

(B) Conversions.

7. Outline a scheme for the following conversions :

(i) Ethane into propane (ii) Acetylene into acetic acid (iii) Methanol into ethanol and vice versa (iv) Acetic acid into propionic acid and vice versa (v) Methylamine from acetic acid (vi) Lactic acid from acetaldehyde (vii) An unsaturated hydrocarbon into a saturated hydrocarbon. (*Panjab Inter 1955*)

8. How will you obtain :

(a) Methyl alcohol from Ethyl alcohol (b) Methane from Ethane (c) Methylamine from Acetamide (d) Acetic acid from propionic acid ? (*Panjab Inter 1962*)

9. How are the following conversions effected :

(a) Benzene to Aniline (b) Aniline to phenol (c) Benzene to Benzaldehyde (d) Toluene to Benzoic acid ? (*Panjab Inter 1962*)

10. (a) Represent the steps by which phenol can be converted into Benzoic acid.

(b) Present a scheme by which Methylamine and Ethylamine can be converted into each other. (*Panjab Inter 1961*)

(ii)

11. Outline a simple and direct scheme (indicating the reagent and the conditions employed) to convert : (i) Toluene into T.N.T. (ii) Benzene into salicylic acid (iii) Benzene into benzamide (iv) Chlorobenzene into benzene (v) Nitrobenzene into azobenzene (vi) Aniline into *p*-nitroaniline (vii) Benzyl alcohol into toluene (viii) Phthalic acid into benzoic acid.
Panjab Inetr 1961

(C) What Happens ?

12. What happens when :

(a) Potassium acetate (or succinate) solution is electrolysed (b) sodium formate is heated (c) Nitrous acid acts on urea and aniline separately (d) Glycerine is heated with oxalic acid (e) Formaldehyde is treated with ammonia (f) Ethyl alcohol is heated with bleaching powder ?
(Rajputana Inter 1959)

13. What happens when :

(i) Hypochlorous acid acts on ethylene (ii) sodium hypobromite acts on urea (iii) Acetyl chloride acts on glycerol ?
(Rajputana Inter 1950)

14. Explain with equations what happens when :

(a) Nitrobenzene is reduced with stannous chloride and alkali (b) Ethyl iodide is heated with (i) alcoholic potash and (ii) aqueous potash (c) Glucose is warmed with phenyl hydrazine in dilute acetic acid solution.
(Delhi Pre-Medical 1960)

15. Write equations and names of the important products when :

(i) Sabatier and Senderen's reaction takes place (ii) Sodium succinate is electrolysed (iii) An alkyl halide reacts with sodium alcoholats (iv) Nitroglycerine explodes (v) Sodium alkoxide is heated with CO under pressure and the product hydrolysed (vi) Tartaric acid is reduced with HI (vii) Biuret reaction takes place (viii) chloroform is oxidised in the excess of oxygen.
Panjab Inter 1960 Sept.)

16. Write equations and names of important products when :

- (i) Ethane is chlorinated in shade.
- (ii) Williamson's synthesis takes place.
- (iii) Ethyl acetate reacts with ammonia.
- (iv) Citric acid is heated to 150°C.
- (v) Acetamide is subjected to Hofmann's bromamide reaction.
- (vi) Ethylamine is heated with chloroform and alcoholic potash.
- (vii) Fructose reacts with acetic anhydride.
- (viii) Sucrose is warmed with dil. mineral acid.
(Panjab Inter 1959)

17. Discuss the changes with equations in the following reactions :

(a) Ethylamine is treated with nitrous acid (b) chlorine is passed through acetic acid (c) glycerol is heated with oxalic acid and (d) tin and hydrochloric acid react with nitrobenzene.
(U. P. Board Inter 1959)

18. Write equations for the reaction between :

(i) Sodium acetate and soda lime (ii) Ethylene and alkaline KMnO_4 (iii) Ethylene absorbed in H_2SO_4 and product boiled with water (iv) Glycerol and oxalic acid at 110°C (v) C and H to form tartaric acid (vi) An alkyl isocyanide and boiling alkali.
(Panjab Inter 1952)

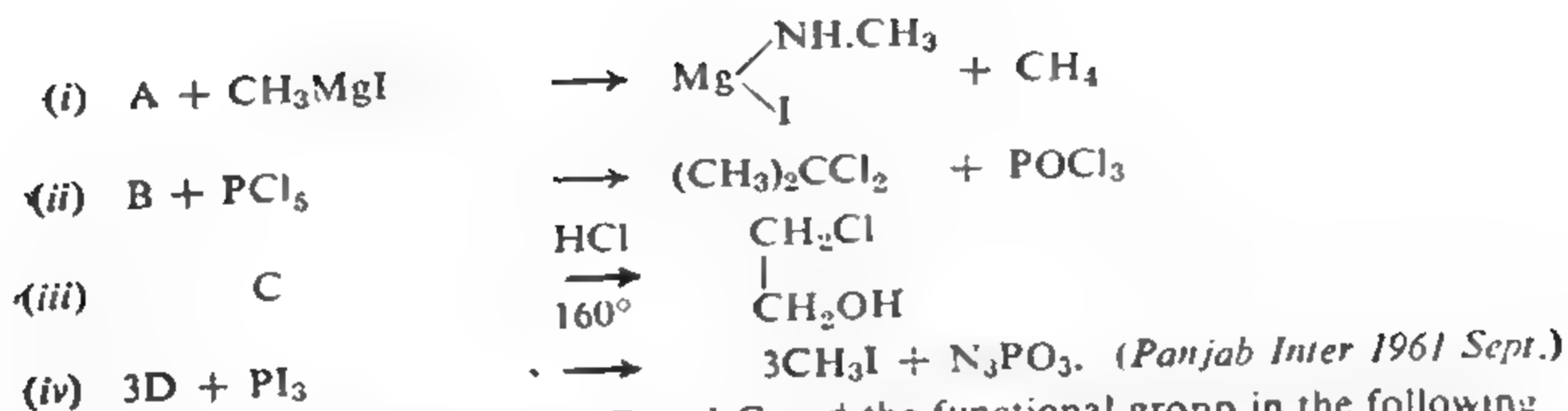
(D) Equations.

19. Give equations and names of products when the following substances react :

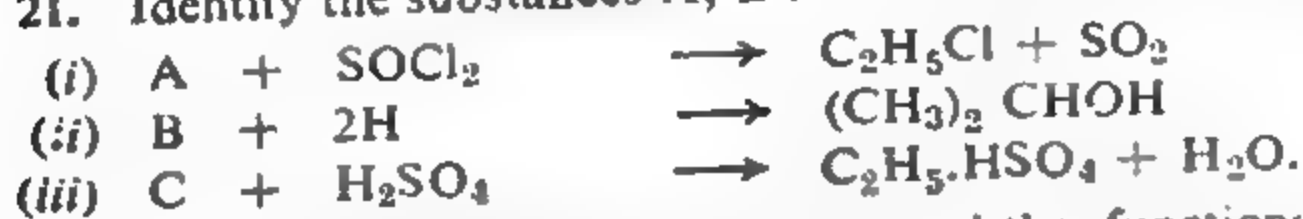
- (a) Formaldehyde with (i) ammonia and (ii) caustic soda (b) acetaldehyde with (i) ammoniacal solution of silver nitrate and (ii) Fehling solution.
- (c) Acetone with (i) chlorine and (ii) phosphorus pentachloride.
Panjab B. Sc. Part I 1962)

20. Name the reactants A, B, C, D and the functional group present therein, in the following equations and write one more characteristic reaction of the group so found :

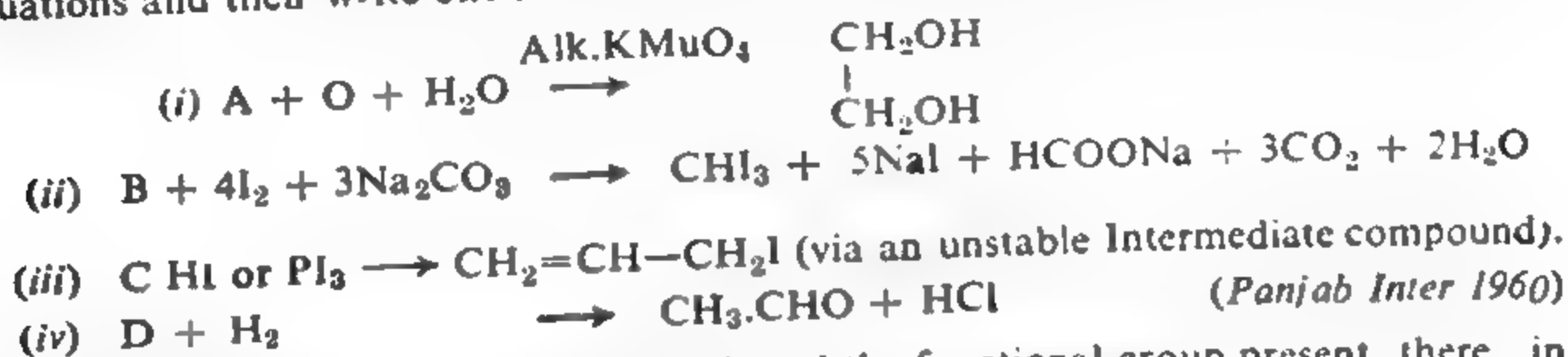
(iii)



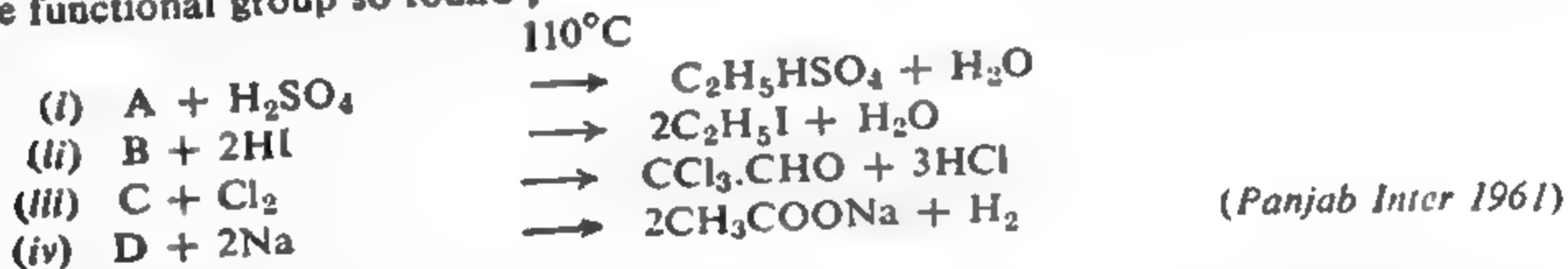
21. Identify the substances A, B and C and the functional group in the following



22. Identify the substance A, B, etc. and the functional group in the following equations and then write one more reaction characteristic of the functional group :



23. Name the reactant A, B, C, and D and the functional group present there, in the following equations. Also write one more characteristic reaction for each of the functional group so found :



(E) Short notes.

24. Explain what is meant by Addition, Polymerisation and Condensation. Illustrate your answer with examples from aldehydes and ketones (Panjab Inter 1962)

25. Explain with the help of one illustrative example in each, what is meant by any four of the following :

(a) Markownikoff's Rule (b) Saponification (c) Hydrogenation of oils (d) Fermentation (e) Optical isomerism. (Panjab Inter 1960)

26. Write short notes on any four of the following :

(a) Sandmeyer's Reaction (b) Perkin's Reaction (c) Schotten-Baumann's Reaction (d) Kolbe's Reaction (e) Cannizzaro's Reaction. (Panjab Inter 1962)

27. Write illustrative but brief notes on any four of the undermentioned :

(i) Polymerisation (ii) Hydrogenation of oils (iii) Optical or stereoisomerism (iv). Descent of a homologous series (v) Monosaccharides (vi) Multiple effect evaporator (Panjab Inter 1959 Sept.)

28. Write about 10 lines on light oil fraction of coal tar distillation or nitration of aromatic compounds and the conditions attending thereto. (Panjab Inter 1959)

29. Write notes on any three of the following :

(a) Fermentation (b) Isomerism (c) Steam distillation (d) Polymerisation (e) Sulphonation. (Jammu & Kashmir 1960)

(iv)

(F) Distinguish between.

30. Give tests to distinguish between.

(a) Aliphatic and aromatic compounds (b) Urea and acetamide (c) phenol and ethyl alcohol (d) Methyl alcohol and ethyl alcohol (e) Cane sugar and grape sugar (f) Oxalic acid and tartaric acid.

Show that you understand the chemical reactions on which the tests are based.

(Rajputana Inter 1952)

31. How will you distinguish between :

(a) Urea and acetamide (b) Tartaric acid and oxalic acid (c) Methyl alcohol and ethyl alcohol (d) Glycerine and concentrated cane-sugar solution (e) Vegetable oil and kerosene oil ?

(Rajputana Inter 1960)

32. How will you detect that :

(a) A given solution contains acetic acid or formic acid.

(b) A given liquid is aniline or phenol.

(c) A given powder is benzoic acid.

(d) A given powder is glucose, and

(e) A given liquid is benzene

(U.P. Board Inter 1953)

33. Give two distinguishing chemical reactions of the following pairs of compounds :

(a) Methylamine and dimethylamine (b) Formic acid and acetic acid (c) Benzaldehyde and acetaldehyde (d) Glucose and oxalic acid.

(Delhi pre-medical 1960)

34. Give the tests by which primary, secondary and tertiary amines can be distinguished from one another. How will you get methylamine from acetic acid ?

(Panjab B.Sc. Part 1962)

(G) Preparations.

35. Give the preparation and two uses of ;

Acetanilide or Aspirin ; Picric acid or salicylic acid. (Panjab Inter 1961 part I)

36. Describe the preparation, properties and uses of trichloro methane.

(Panjab Inter 1962)

37. Describe the preparation of pure nitrobenzene. How will you obtain (i) Phenol and (ii) Azobenzene from nitrobenzene ?

(Panjab T.D.C. Part I 1962)

38. How can a halogen atom be introduced in (i) the side chain and (ii) the nucleus of an aromatic hydrocarbon ? Describe the difference in chemical behaviour of the compounds formed. Why is it that iodo derivatives cannot be prepared by direct iodination ? How is the difficulty overcome ?

(Panjab T.D.C. Part I 1962)

39. Describe the laboratory preparation of any three of the following : Diethyl ether, ethyl acetate, nitrobenzene, toluene.

(Delhi Pre-medical 1960)

40. What is fermentation ? Discuss the preparation of ethanol and lactic acid by this method.

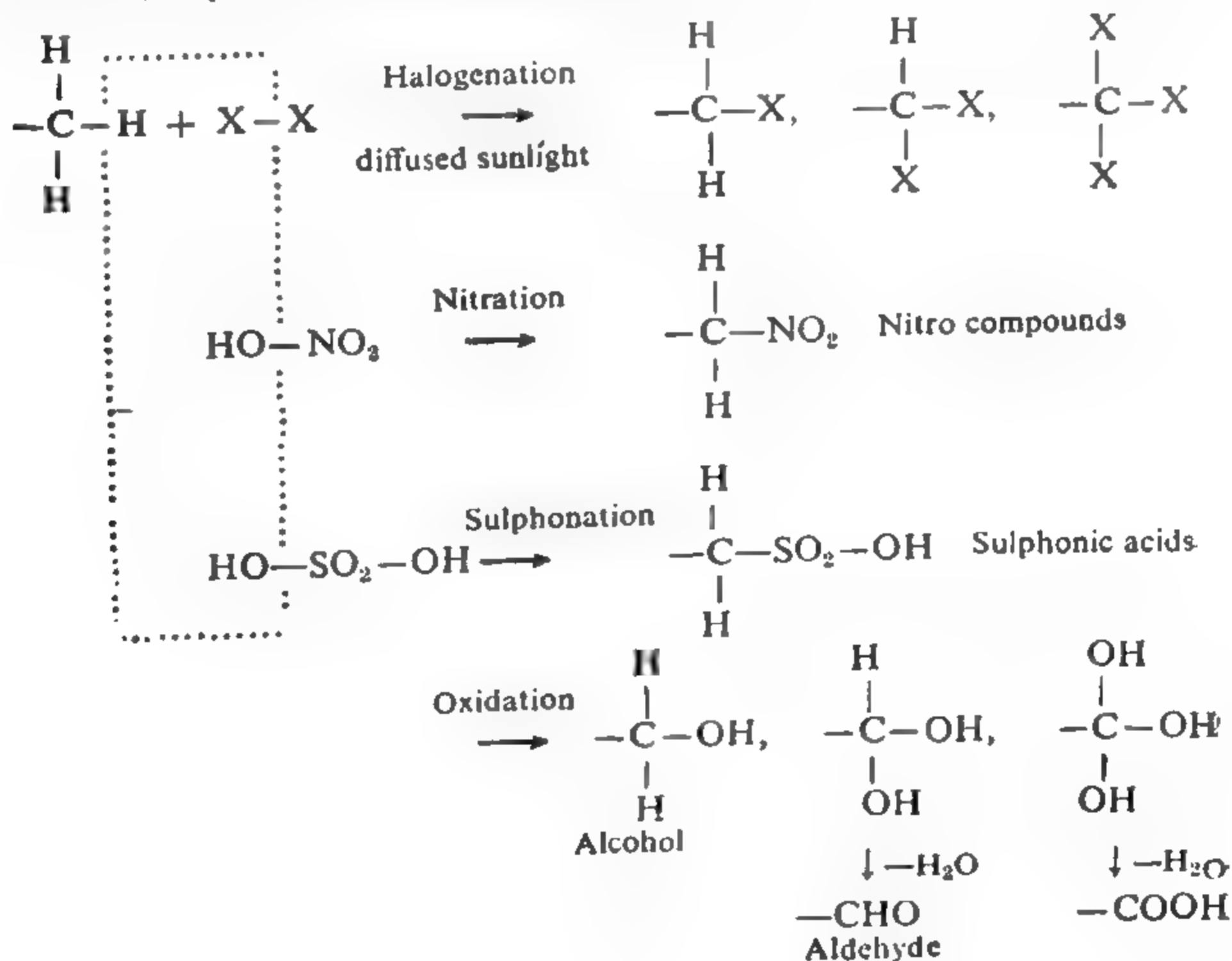
(Delhi Pre-medical 1960)

APPENDIX

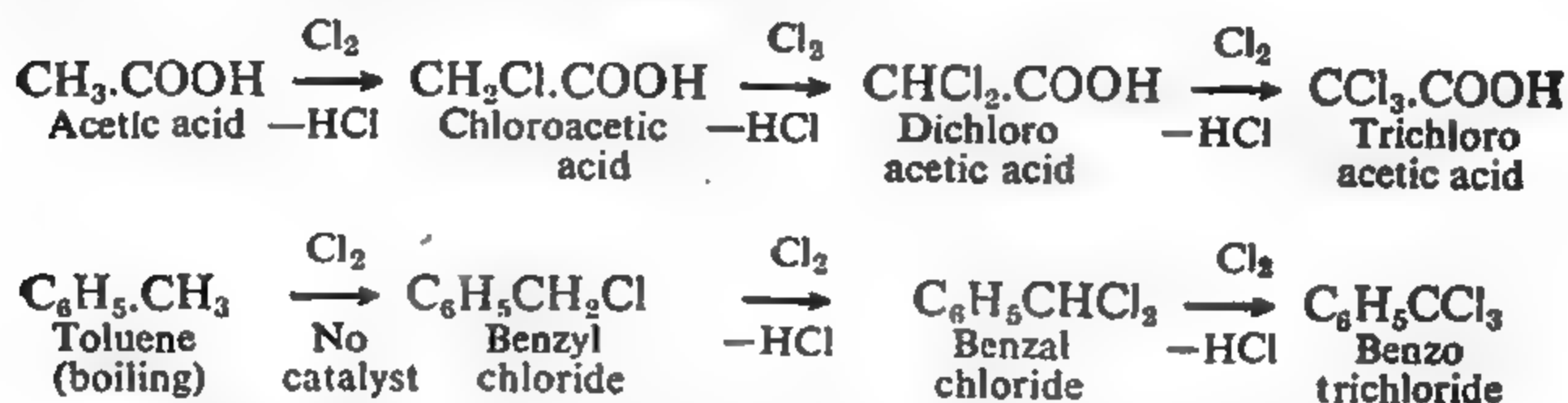
TYPICAL REACTIONS OF VARIOUS FUNCTIONAL GROUPS

More than a million organic compounds are known at present and this number is increasing at the rate of about 5 per cent per annum. It is impossible for anyone to remember all of them along with their characteristic properties. Fortunately, however, all these compounds fall into different categories depending upon the nature of their functional groups. In the present chapter, therefore, the typical reactions of some important functional groups have been discussed. This small chapter will help the students to gather conveniently and economically the most essential and basic information regarding most of the organic compounds. This is also likely to be useful for a quick revision. Wherever possible, the difference in the properties of a particular group, when present in an aliphatic or an aromatic compound, has been pointed out. For exact conditions of reactions, reference is to be made to the previous pages.

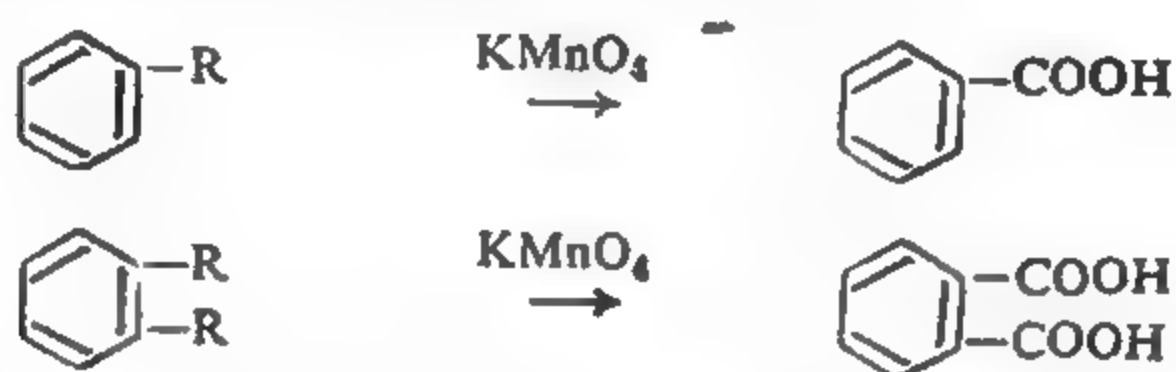
The Alkyl Group, $-R$. The monovalent alkyl groups, such as methyl ($-\text{CH}_3$), ethyl ($-\text{C}_2\text{H}_5$), etc., are present in almost all aliphatic compounds. They comprise of $\text{C}-\text{H}$ and/or $\text{C}-\text{C}$ bonds. Normally, these bonds are quite stable. Under *suitable conditions*, however, the alkyl groups undergo **substitution reactions**, such as *halogenation*, *nitration*, *sulphonation* and *oxidation*. Thus :



The *most characteristic reaction* of the alkyl group, however, is **halogenation**. Thus, the alkyl group present in any compound will respond to substitution by halogens, e.g.,

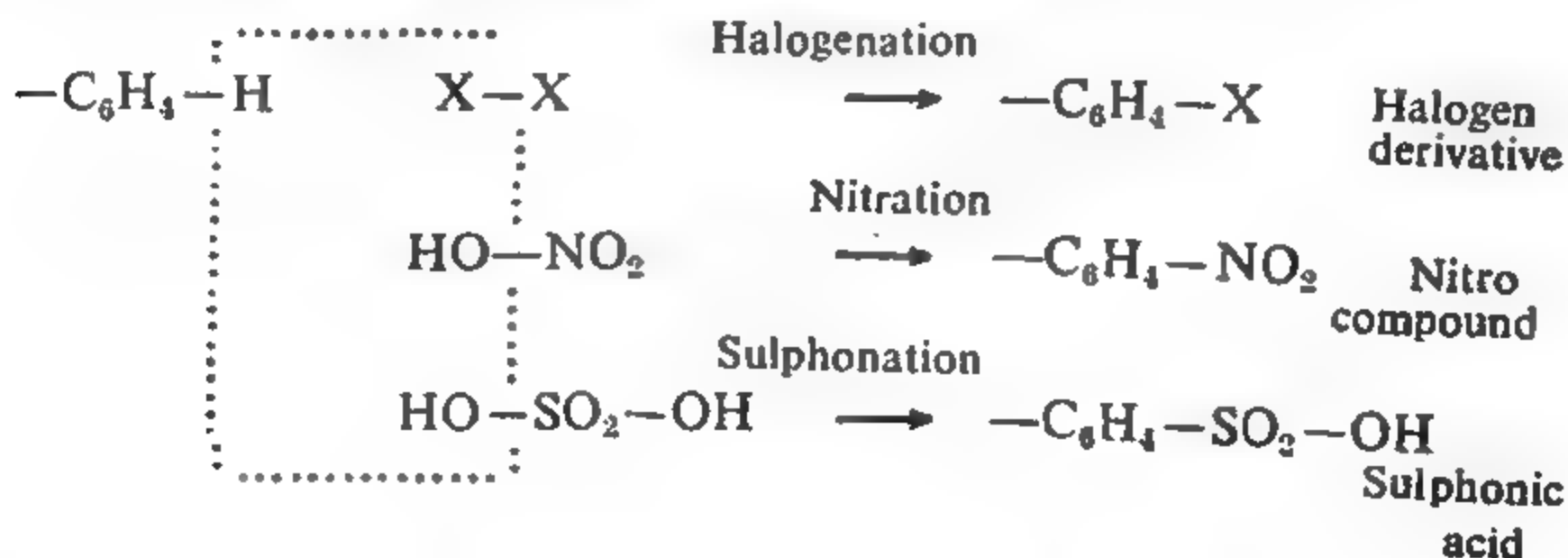


Note. An alkyl group, attached to an aromatic nucleus on treatment with acidified KMnO_4 gets *oxidised* to —COOH group, whatever may be the length of the alkyl group.



(*R* may be —CH_3 or $\text{—C}_2\text{H}_5$ or $\text{—C}_3\text{H}_7$, etc.,)

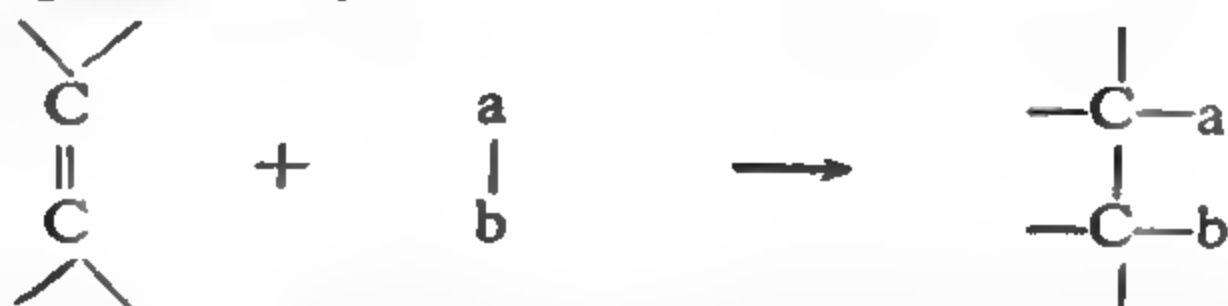
The Aryl Group. The aryl group, $\text{C}_6\text{H}_5\text{—}$ (phenyl), present in most of the aromatic compounds is the benzene ring bereft of a hydrogen atom and hence it shows the *typical substitution reactions of the benzene nucleus*, such as halogenation, nitration, sulphonation. The positions taken by the substituents will, evidently, depend upon the nature of the group attached to the aryl group (*cf.* orientation rule). Further, if the group attached is ortho and para-directing, substitution takes place easily and if it is meta-directing, more drastic conditions are required.



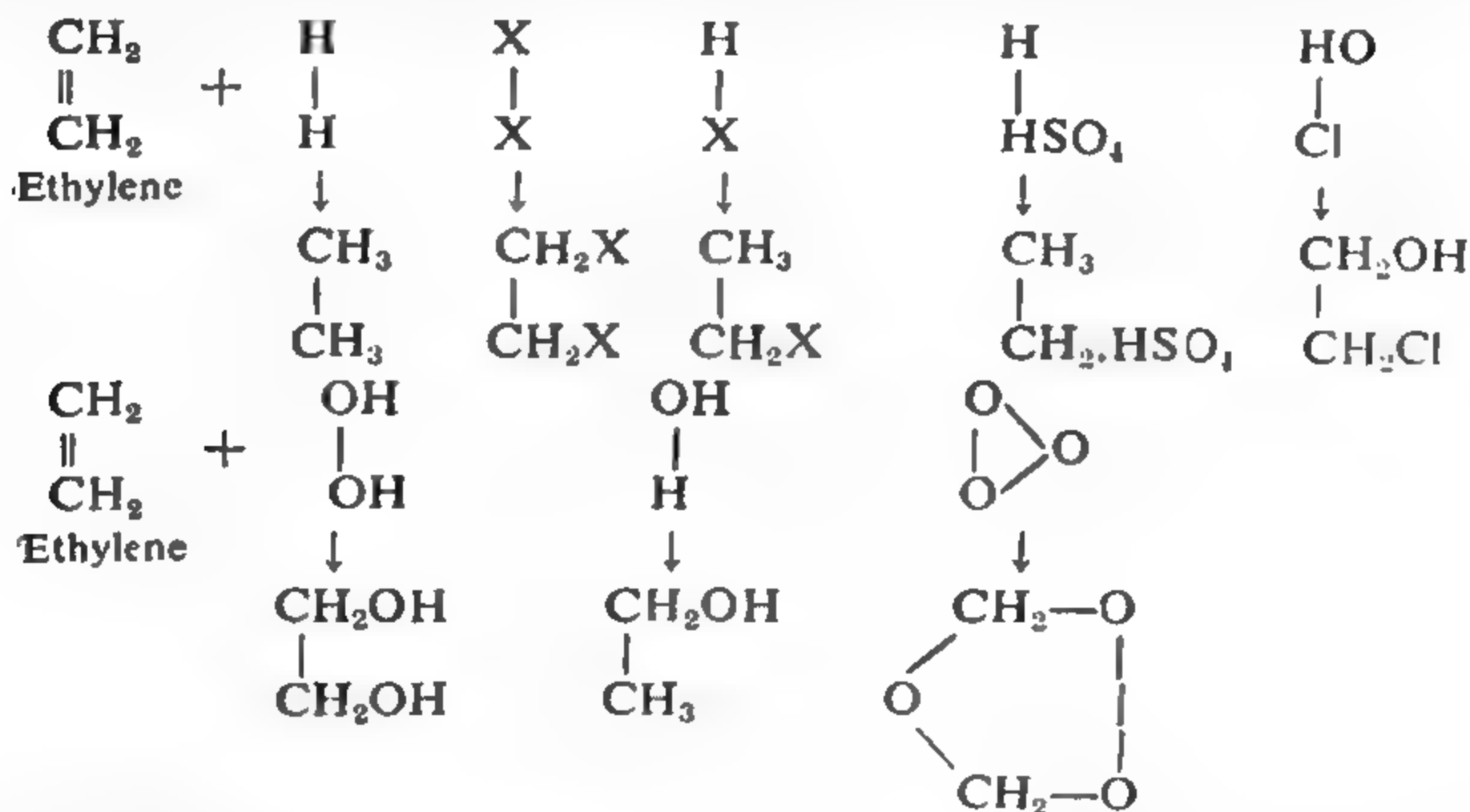
Further substitution is also feasible depending upon the conditions.

The Olefinic Group. >C=C< . Olefinic group is a sign of unsaturation. The characteristic property of the group is **addition**,

represented in a general way as

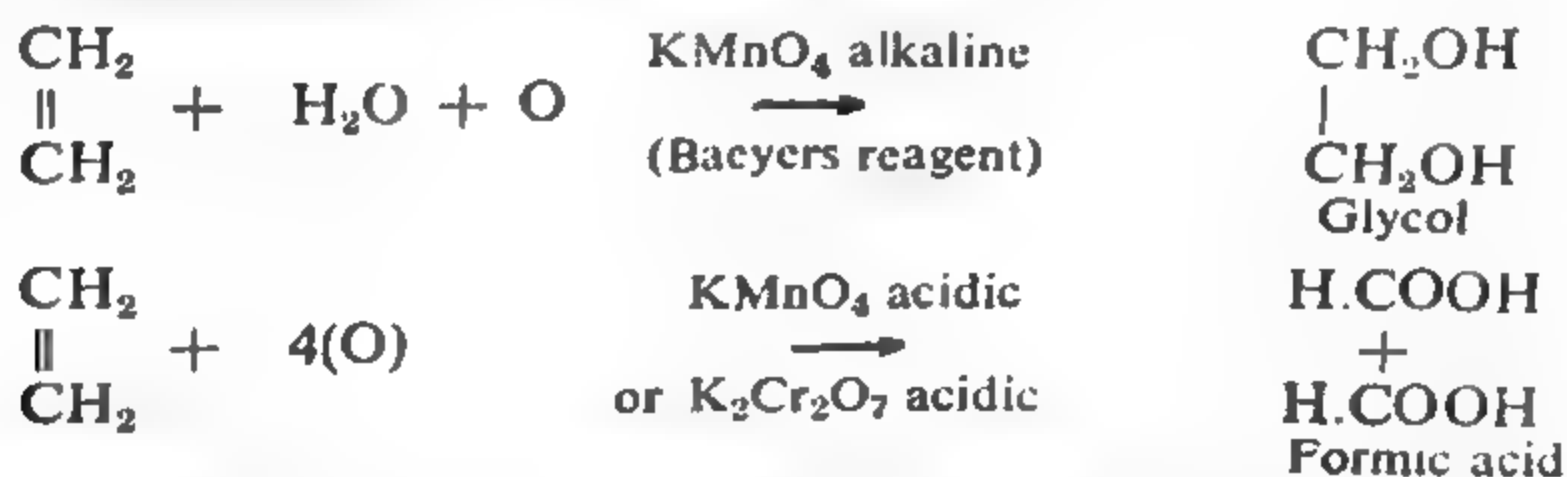


Thus, ethylene, a typical member of the olefins, forms addition products with hydrogen, halogens, halogen acids, sulphuric acid, hypochlorous acid, hydrogen peroxide, ozone, etc., under suitable conditions :



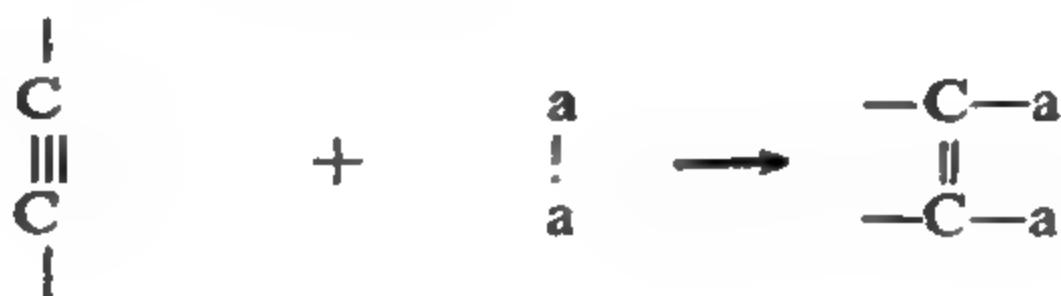
(X=Cl, Br, I)

Another characteristic property of the olefinic group is its easy attack by oxidising agents, *e.g.*,

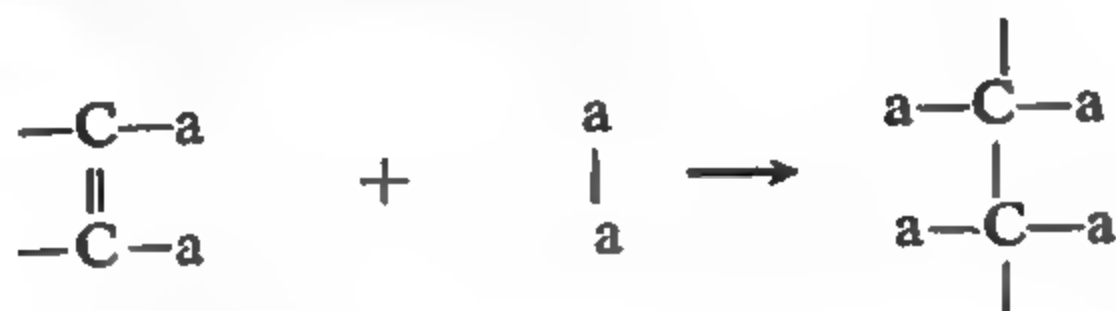


The Acetylenic Group, $-\text{C}\equiv\text{C}-$. Acetylenic group indicates greater unsaturation and greater reactivity even than the olefinic group. The characteristic property is again addition represented in a general way as :

(i) Addition of one molecule.



(ii) Addition of second molecule



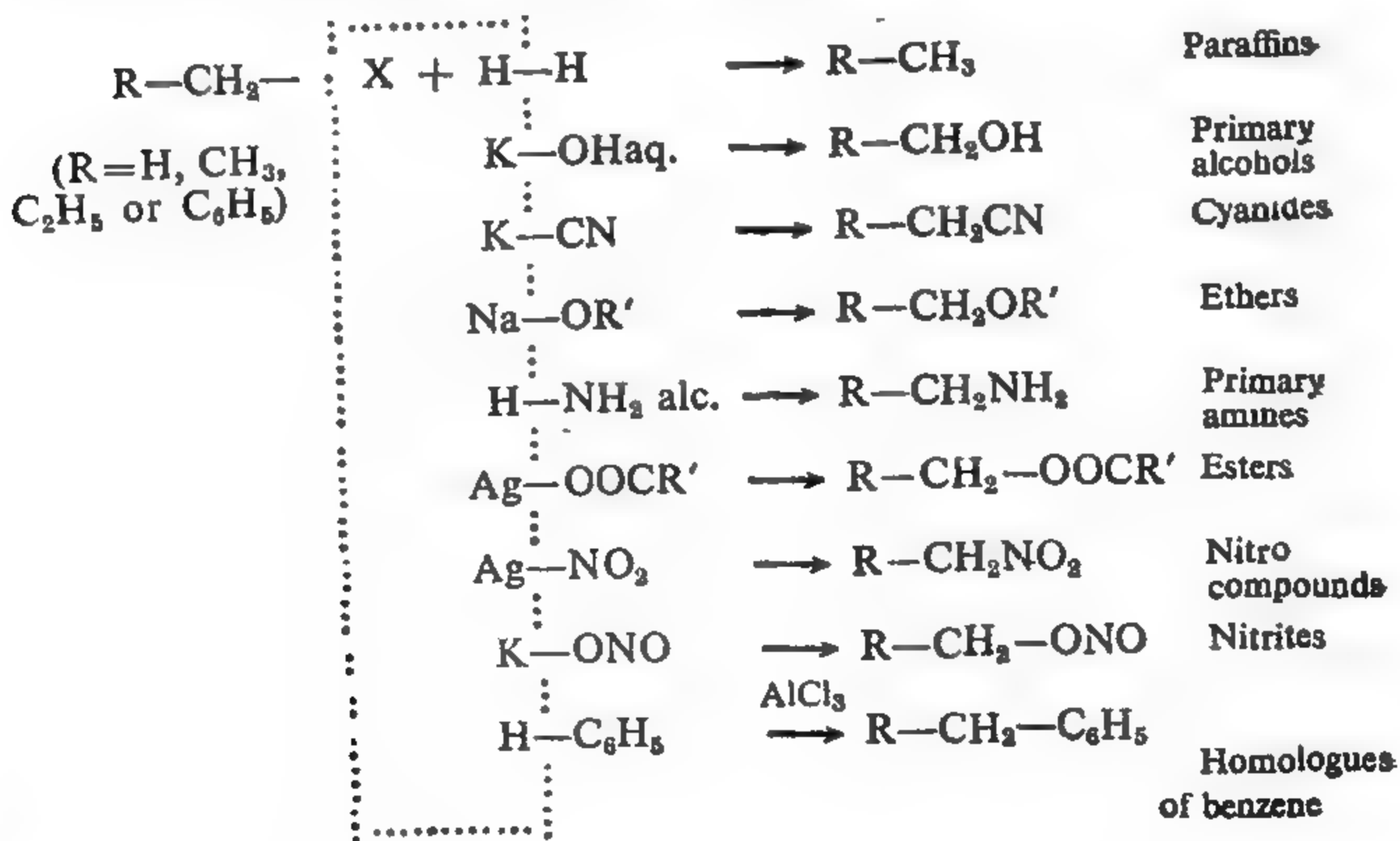
The addition of second molecule in case of unsymmetrical molecules (e.g., HX) takes place according to *Markownikoff's rule*.

The acetylenic group is also readily attacked by oxidising agents, e.g.,

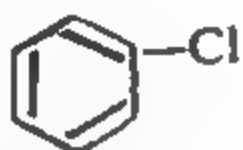


Note. Compounds containing olefinic and acetylenic groups undergo polymerisation giving different products under different conditions.

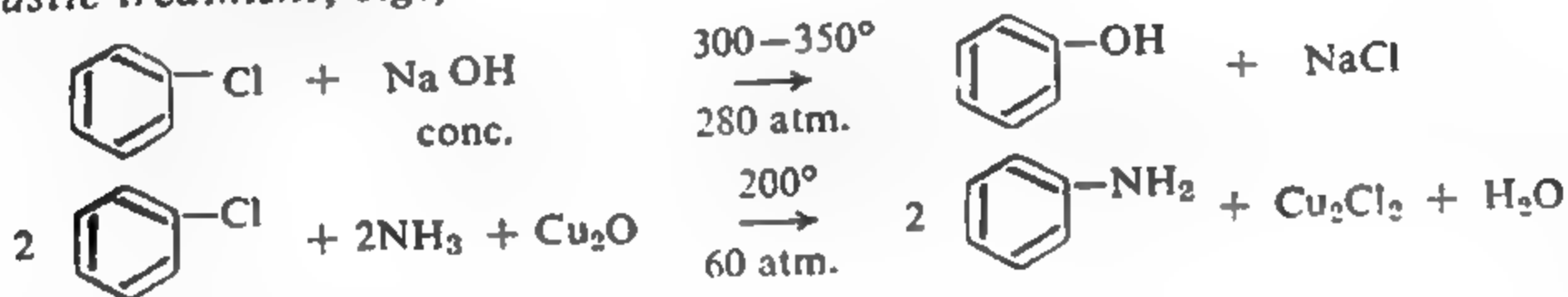
The Halogen Group, —X. (Cl, Br, I). (i) The halogen group present in the structure, —C—C—X, i.e., in alkyl halides (e.g., CH₃—X, CH₃—CH₂—X, CH₃—CH₂—CH₂—X) or aryl substituted alkyl halides (e.g., C₆H₅—CH₂—X), is in loose combination with the carbon atom and is readily replaced by almost all other groups. Thus :



(ii) The halogen group present in the structure $-\text{C}=\text{C}-\text{X}$, as in vinyl chloride, $\text{CH}_2=\text{CH}-\text{Cl}$ or chlorobenzene,

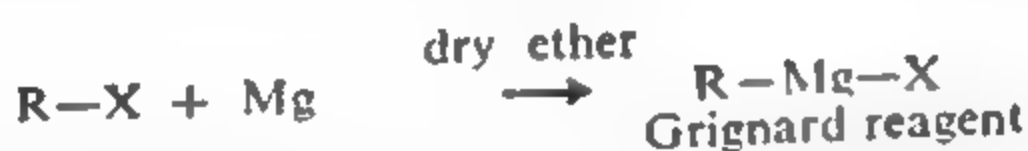


is firmly held by the carbon atom and is not *easily* replaced. Thus, the reagents like KOH aq., KCN , RONa , NH_3 , AgNO_2 , KNO_2 , etc., do not react. The halogen group in such cases can be replaced only on a *drastic treatment*, e.g.,




and so on.

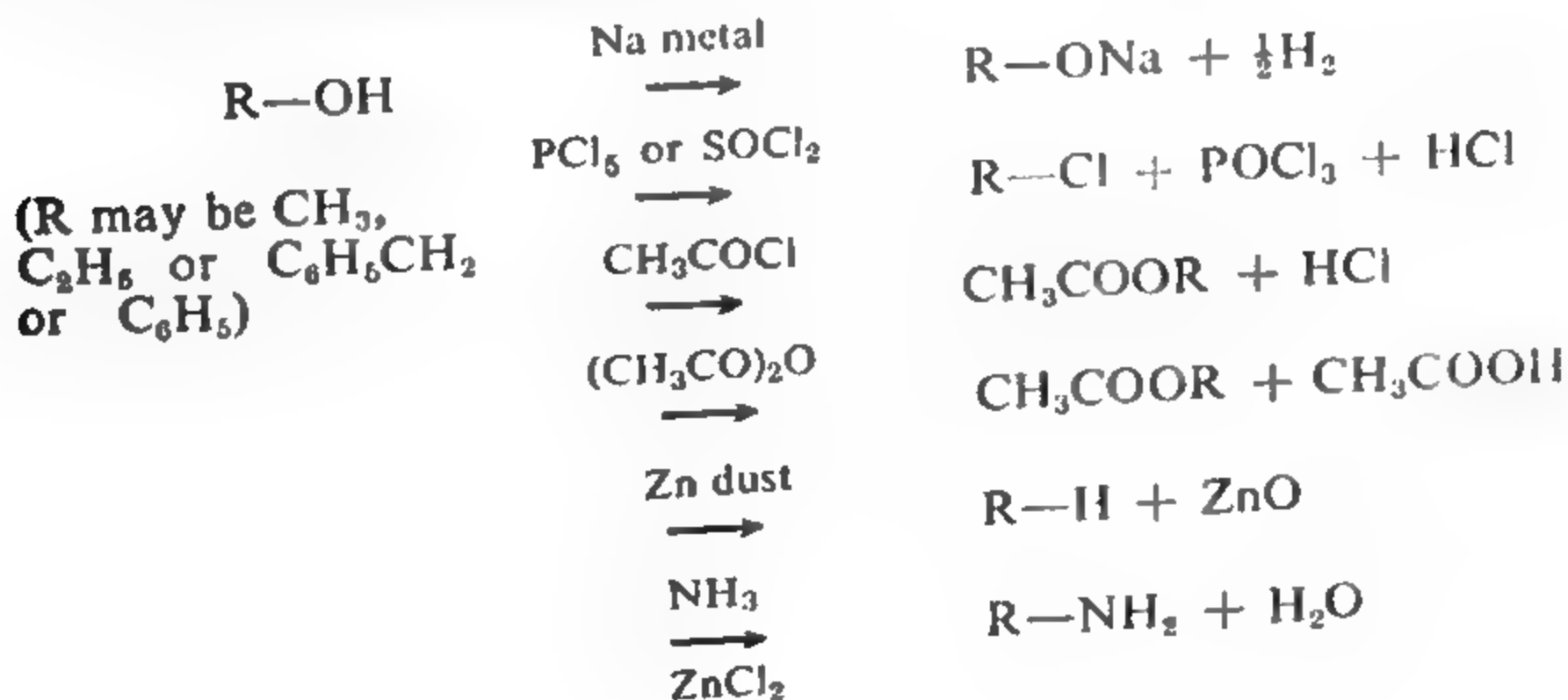
(iii) The following reactions are given whether the halogen group is present in the structure $-\text{C}-\text{C}-\text{X}$ or $-\text{C}=\text{C}-\text{X}$:



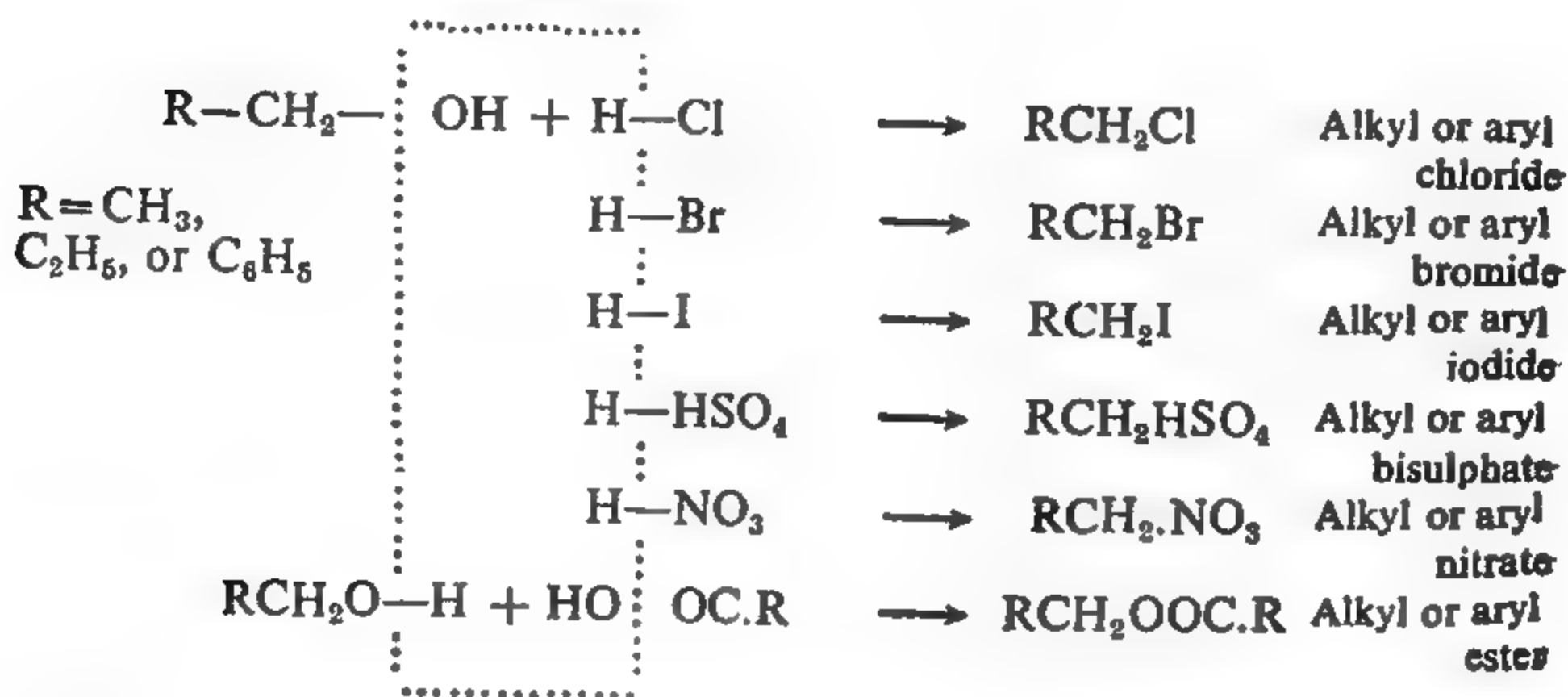
(R may be CH_3 , C_2H_5 , or C_6H_5 , $\text{C}_6\text{H}_5\text{CH}_2$)

The Hydroxyl Group, $-\text{OH}$. The hydroxyl group when present in aliphatic compounds (e.g., methyl alcohol, CH_3OH , ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$) or in aryl substituted aliphatic compounds (e.g., benzyl alcohol, $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$) is called **alcoholic hydroxyl** and when directly linked to the benzene nucleus (e.g., phenol, ) it is called the **phenolic hydroxyl**.

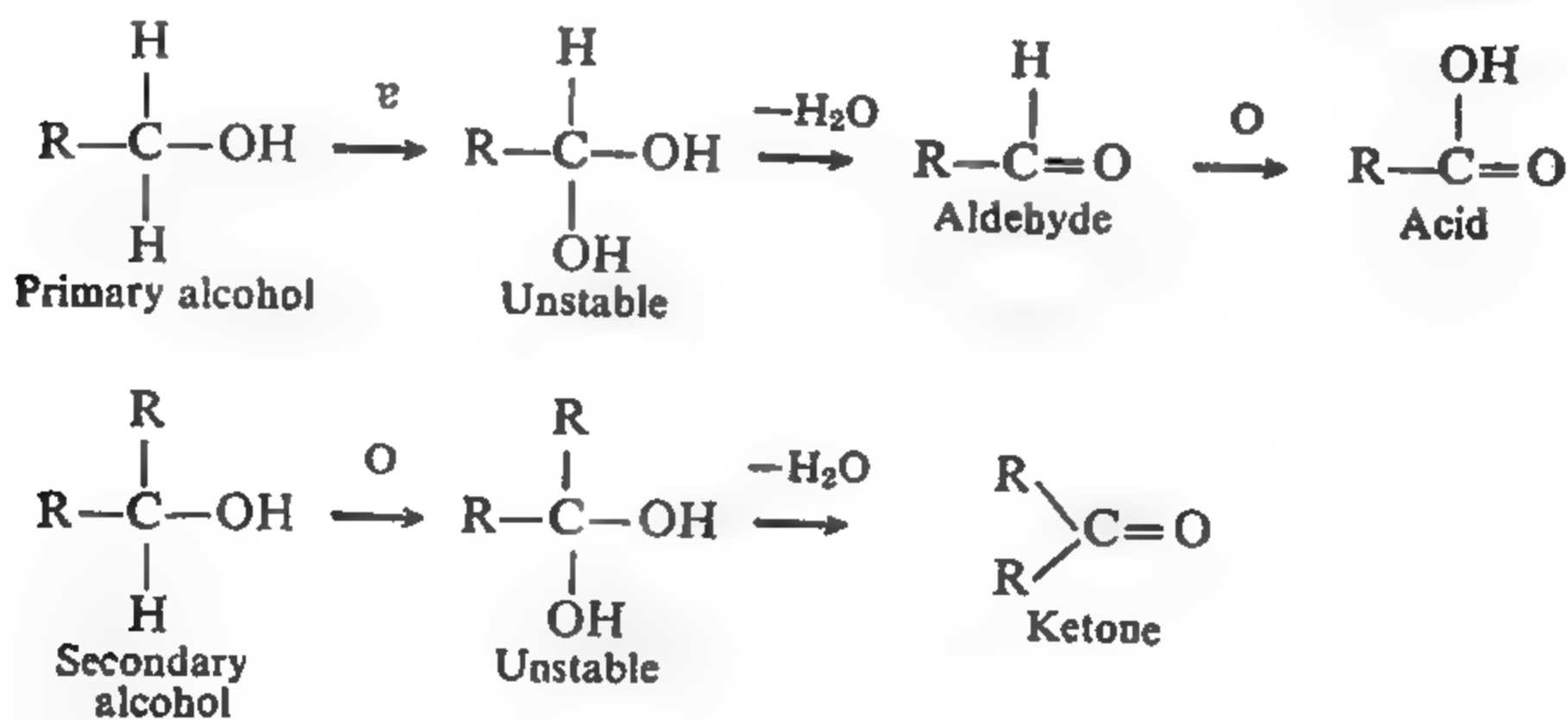
(i) The hydroxyl group (whether alcoholic or phenolic) gives the following typical reactions:



(ii) The alcoholic hydroxyl group, however, differs from phenolic hydroxyl group in many respects. (cf. comparison of alcohols with phenols). Thus, the *formation of esters with acids* is a reaction typical only of alcoholic hydroxyl group :



Another typical property of the alcoholic hydroxyl group, when present as primary or secondary alcoholic group, is its **oxidation** :

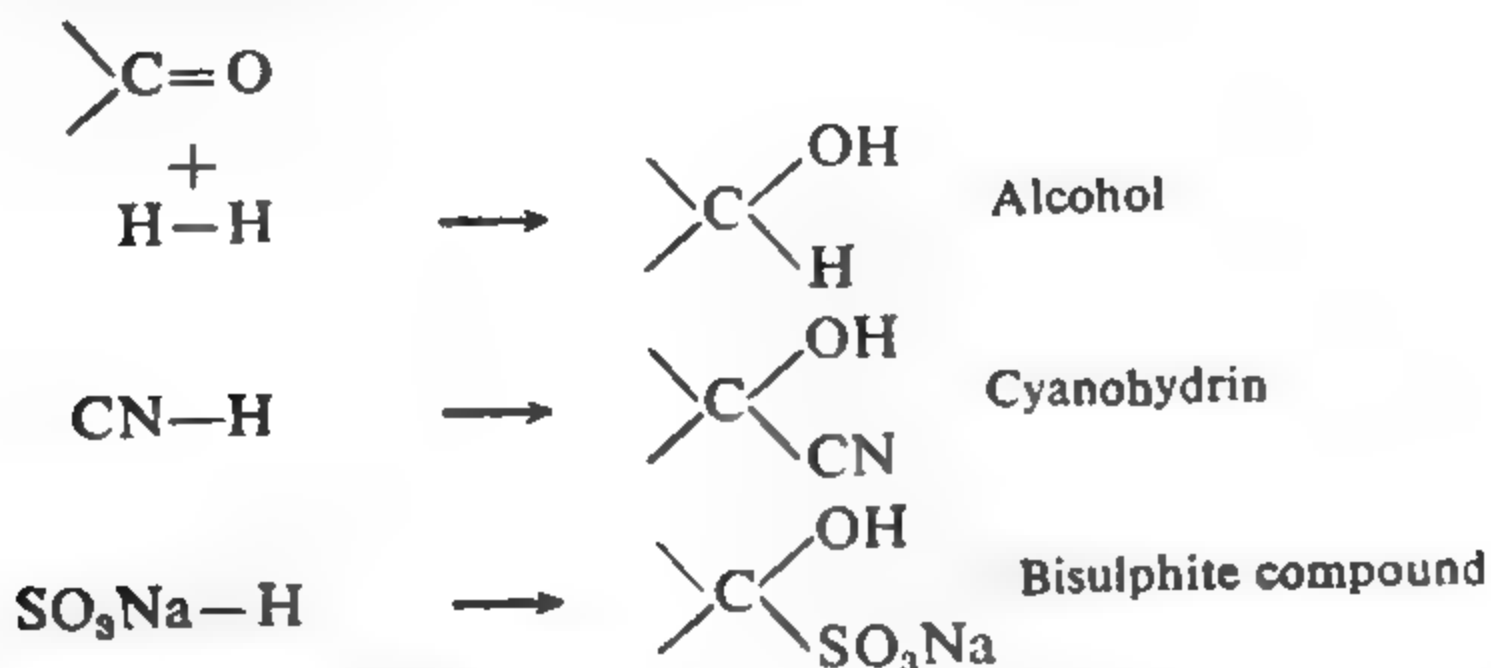


(iii) The following reactions are typical only of phenolic hydroxyl group :

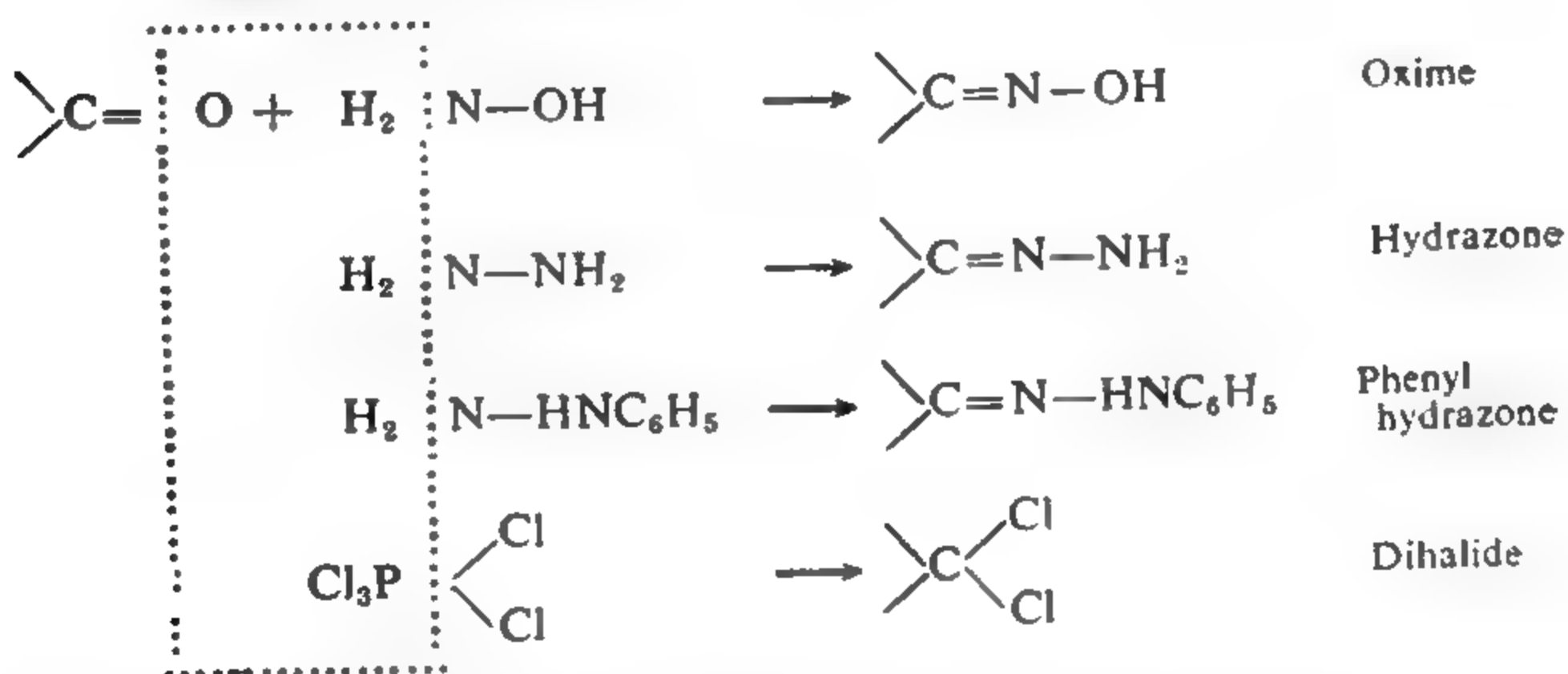


The Carbonyl Group, >C=O . The carbonyl group, >C=O , is present in aldehydes and ketones. The following reactions are typical of the carbonyl group, whether present in aldehydes or in ketones.

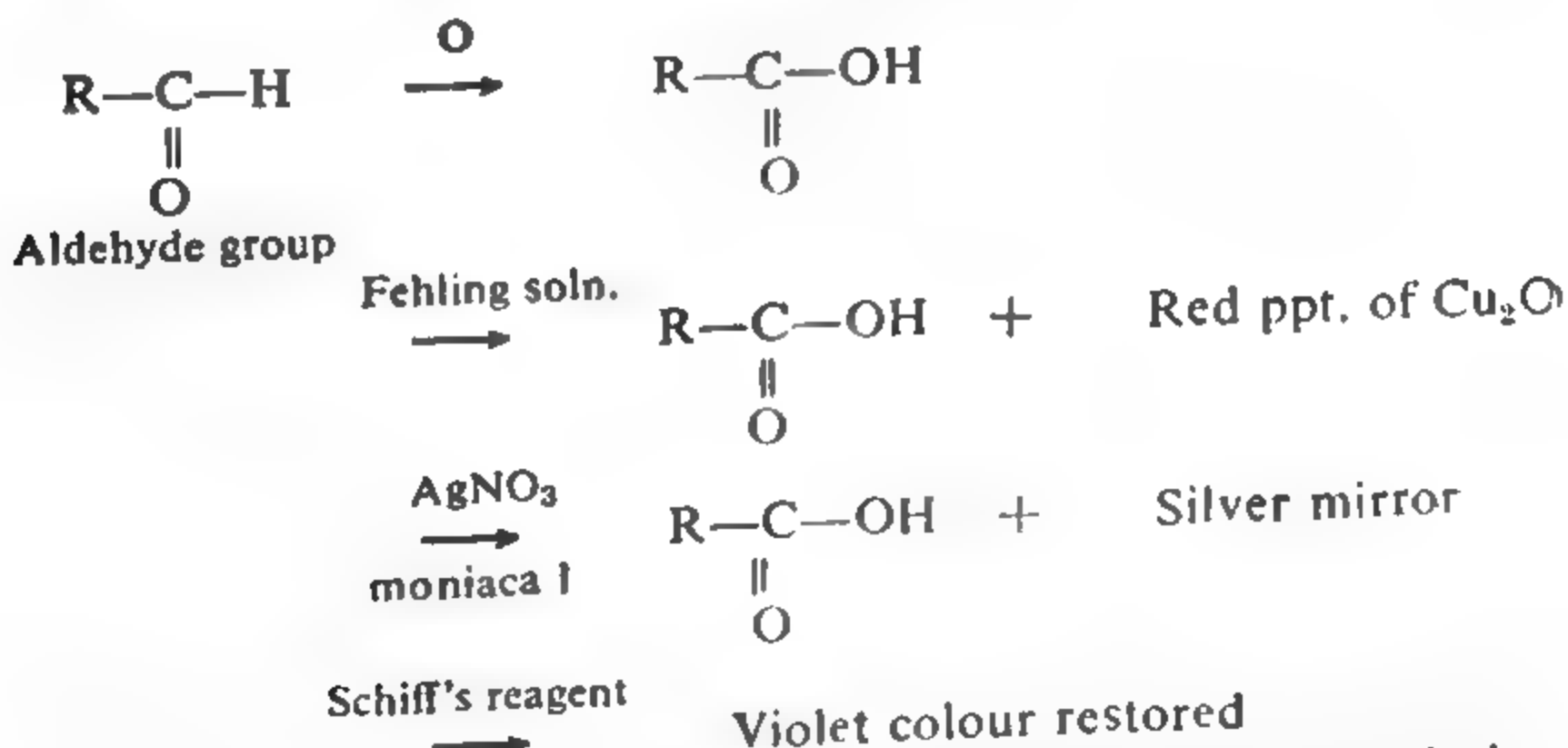
(1) Addition Reactions.



(2) Replacement Reactions.

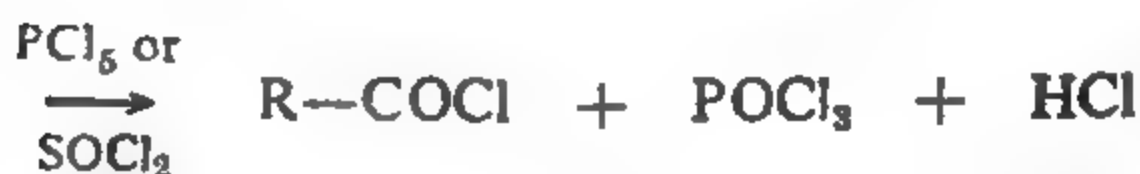


The following reactions are typical of the carbonyl group when it is present in the form of an aldehyde group, $\begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \parallel \\ \text{O} \end{array}$:



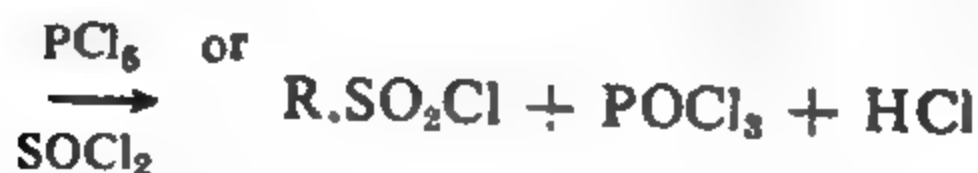
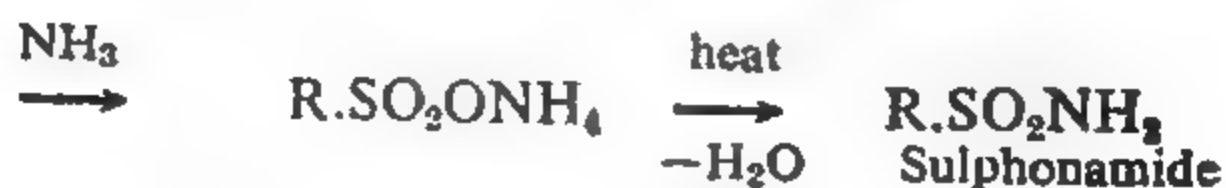
(R may be H, CH₃, C₂H₅ or C₆H₅, C₆H₅CH₂. Fehling solution, however, is not reduced by benzaldehyde.)

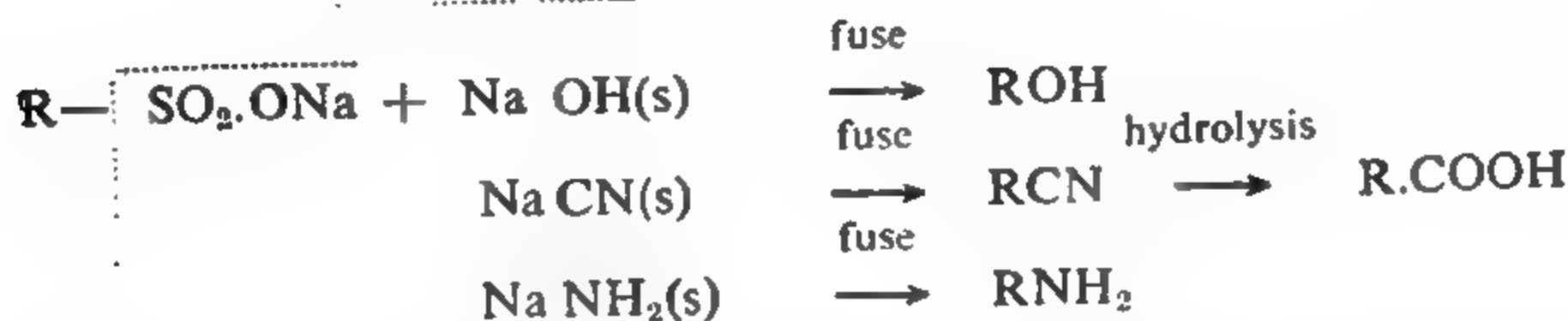
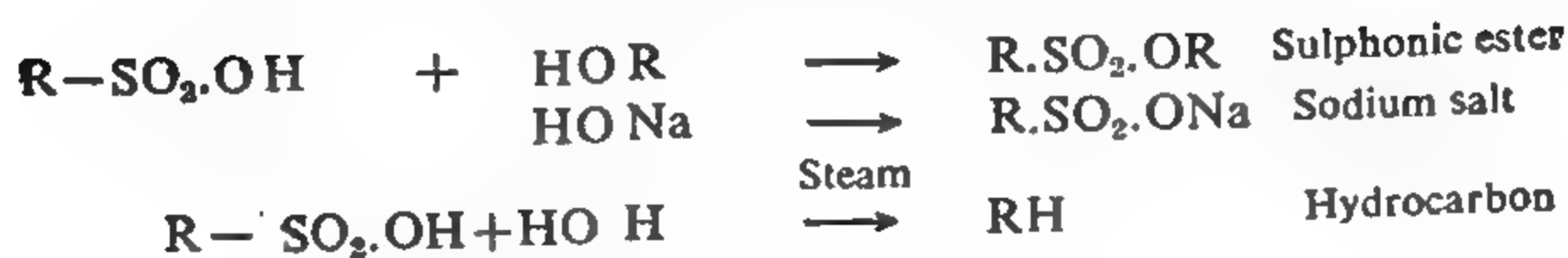
The Carboxyl Group, $-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array}$ The following reactions are typical of carboxyl group.



(R may be $\text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$ or C_6H_5)

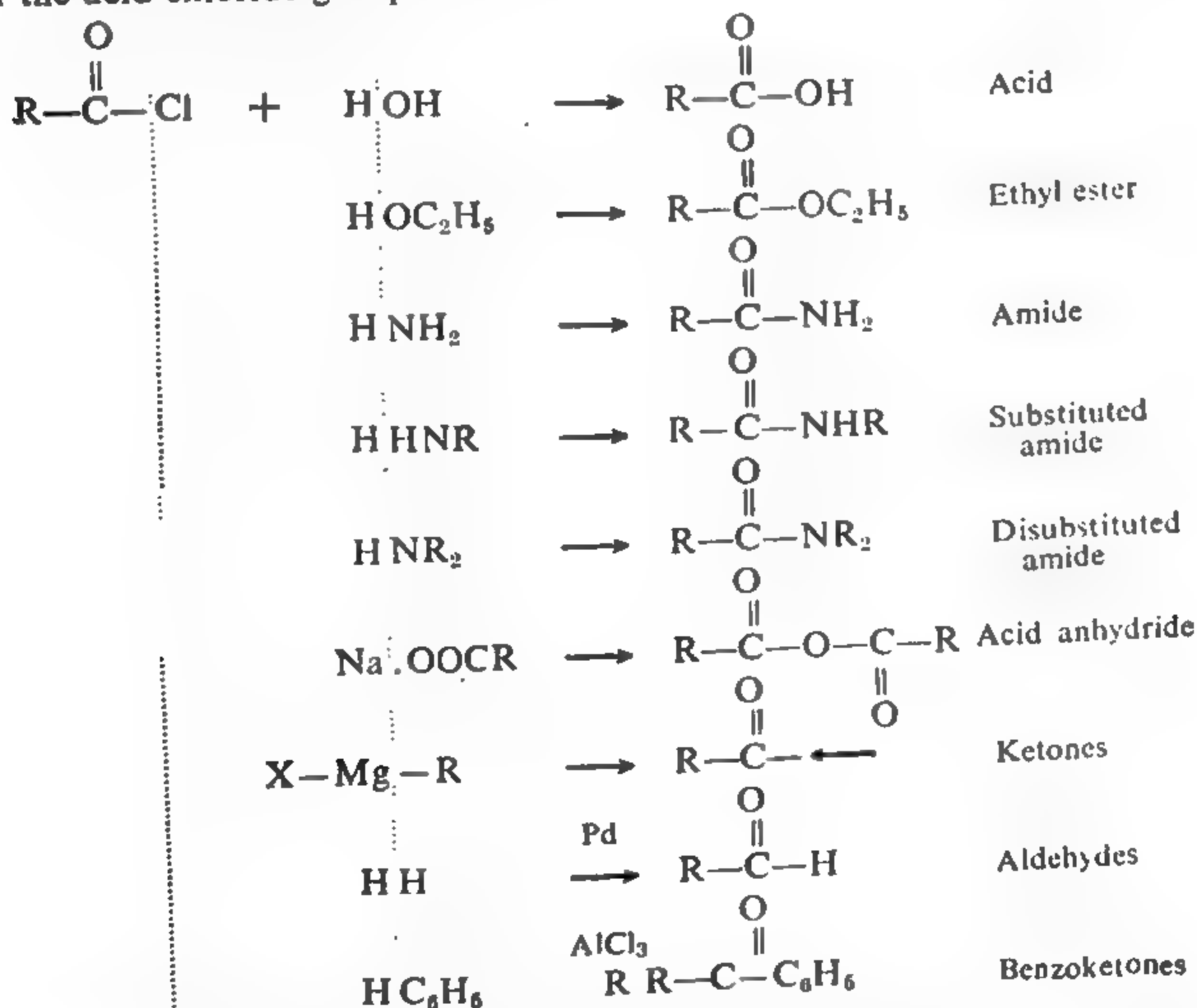
The Sulphonic Acid Group, $-\text{SO}_2\text{OH}$. The sulphonic acid group may be contained in aliphatic or aromatic compounds. Aromatic sulphonic acids are more important. The following reactions are typical of sulphonic acid group. They are, however, more representative of sulphonic acid group in aromatic compounds :





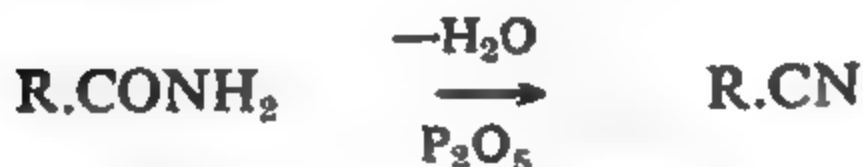
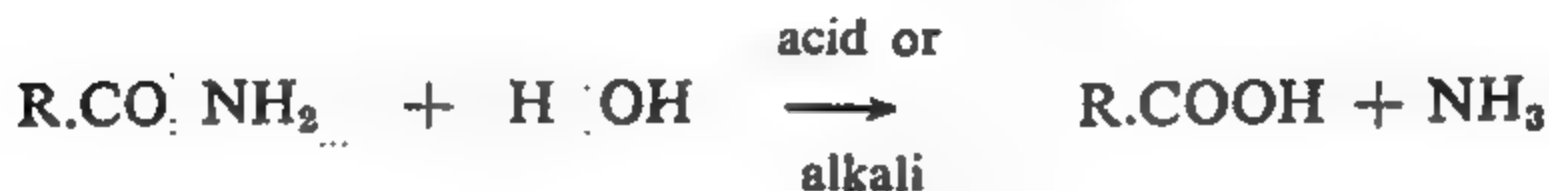
(R in this case stands for C_6H_5 . It may also stand for higher alkyl radicals such as hexyl, heptyl, etc.)

Acid Chloride Group, $-\text{C}(=\text{O})\text{Cl}$. The following reactions are typical of the acid chloride group.

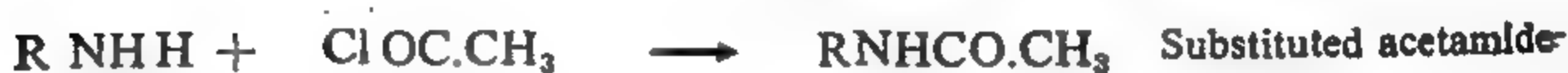
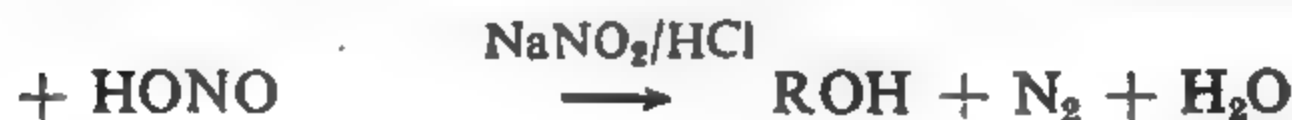


These reactions are reminiscent of the typical reactions of halide groups (cf. page 674).

Acid Amide Group, $\text{—}\overset{\text{O}}{\parallel}\text{C—NH}_2$. The following reactions are typical of the amide group :



The Amino Group, —NH_2 . All primary amines, whether aliphatic or aromatic, contain the functional group, —NH_2 . The following reactions are typical of the primary amino group :



(R = CH_3 , C_2H_5 ... C_6H_5 , $\text{C}_6\text{H}_5\text{CH}_2$)

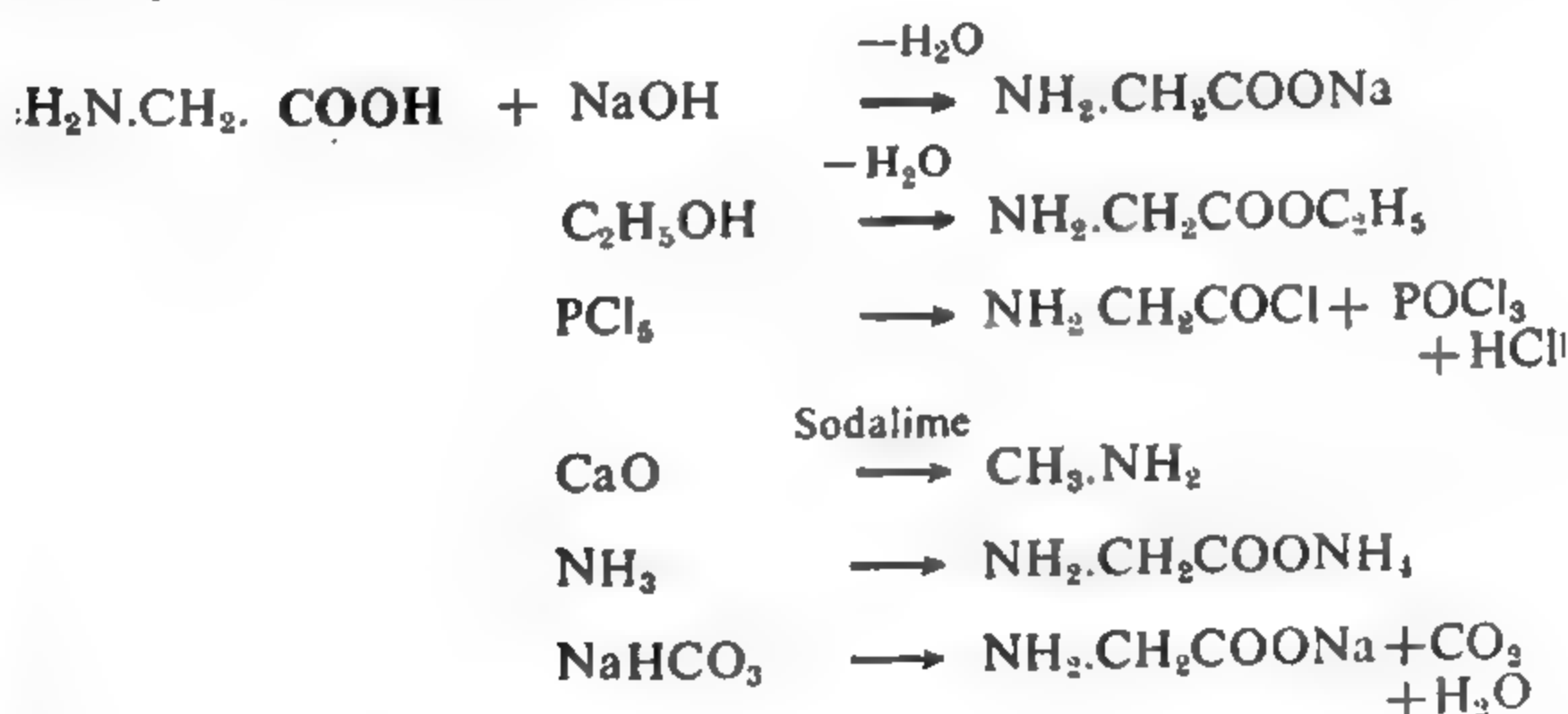
The reaction of $\text{NaNO}_2 + \text{HCl}$ with aniline is different. We get benzene diazonium chloride. At high temperature, however, the reaction is similar. Also, aniline does not give OH^- ions with water.)

Compounds containing more than one functional groups. Many compounds contain more than one functional groups, e.g., glycine, (amino acetic acid), $\text{NH}_2\cdot\text{CH}_2\cdot\text{COOH}$; chloroacetic acid, $\text{Cl}\cdot\text{CH}_2\cdot\text{COOH}$; hydroxy acetic acid, $\text{HO}\cdot\text{CH}_2\cdot\text{COOH}$; lactic acid, $\text{CH}_3\cdot\text{CHOH}\cdot\text{COOH}$;

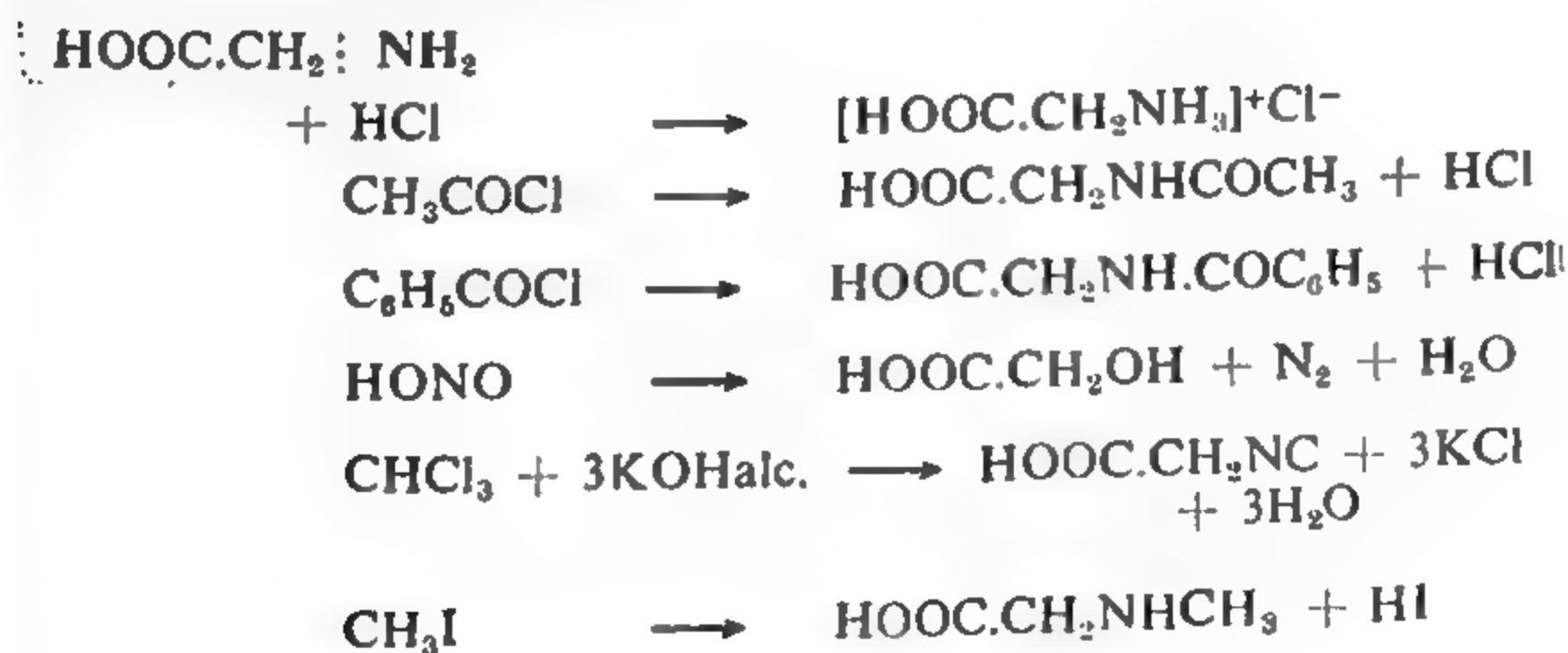
salicylic acid ; salicylaldehyde,  etc.

These compounds *generally* give typical reactions of both the functional groups. For example, amino acetic acid gives the reactions typical of an amino as well as of carboxyl group, as shown below:

Reactions of $-\text{COOH}$ group.



Reactions of $-\text{NH}_2$ group.



LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	8	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4880	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5379	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS—Continued

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56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1 2 2	3 4 5	5 6 7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1 2 2	3 4 5	5 6 7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1 1 2	3 4 4	5 6 7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1 1 2	3 4 4	5 6 7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1 1 2	3 4 4	5 6 6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1 1 2	3 4 4	5 6 6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1 1 2	3 4 4	5 6 6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1 1 2	3 4 4	5 5 6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1 1 2	3 4 4	5 5 6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1 1 2	3 4 4	5 5 6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1 1 2	3 4 4	5 5 6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1 1 2	3 4 4	5 5 6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1 1 2	3 4 4	5 5 6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1 1 2	2 3 4	4 5 6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1 1 2	2 3 4	4 5 6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1 1 2	2 3 4	4 5 5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1 1 2	2 3 4	4 5 5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8687	1 1 2	2 3 4	4 5 5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1 1 2	2 3 4	4 5 5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1 1 2	2 3 3	4 5 5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1 1 2	2 3 3	4 5 5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1 1 2	2 3 3	4 4 5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1 1 2	2 3 3	4 4 5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1 1 2	2 3 3	4 4 5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1 1 2	2 3 3	4 4 5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1 1 2	2 3 3	4 4 5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1 1 2	2 3 3	4 4 5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2	2 3 3	4 4 5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1 1 2	2 3 3	4 4 5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1 1 2	2 3 3	4 4 5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1 1 2	2 3 3	4 4 5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0 1 1	2 2 3	3 4 4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0 1 1	2 2 3	3 4 4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0 1 1	2 2 3	3 4 4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0 1 1	2 2 3	3 4 4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0 1 1	2 2 3	3 4 4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0 1 1	2 2 3	3 4 4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0 1 1	2 2 3	3 4 4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0 1 1	2 2 3	3 4 4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0 1 1	2 2 3	3 4 4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0 1 1	2 2 3	3 4 4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0 1 1	2 2 3	3 4 4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0 1 1	2 2 3	3 4 4
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ANTILOGARITHMS

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01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	001	111	222
02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	001	111	222
03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	001	111	222
04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	011	112	222
05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	011	112	222
06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	011	112	222
07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	011	112	222
08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	011	112	223
09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	011	112	223
10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	011	112	223
11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	011	122	223
12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	011	122	223
13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	011	122	233
14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	011	122	233
15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	011	122	233
16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	011	122	233
17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	011	122	233
18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	011	122	233
19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	011	122	333
20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	011	122	333
21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	011	222	333
22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	011	222	333
23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	011	222	334
24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	011	222	334
25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	011	222	334
26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	011	223	334
27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	011	223	334
28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	011	223	344
29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	011	223	344
30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	011	223	344
31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	011	223	344
32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	011	223	344
33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	011	223	344
34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	112	233	445
35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	112	233	445
36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	112	233	445
37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	112	233	445
38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	112	233	445
39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	112	233	455
40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	112	234	455
41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	112	234	455
42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	112	234	456
43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	112	334	456
44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	112	334	456
45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	112	334	556
46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	112	334	556
47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	112	334	556
48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	112	344	566
49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	112	344	566

ANTILOGARITHMS

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51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	122	3	4	5	5	6	7
52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	122	3	4	5	5	6	7
53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	122	3	4	5	6	6	7
54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	122	3	4	5	6	6	7
55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	122	3	4	5	6	7	7
56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	123	3	4	5	6	7	8
57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	123	3	4	5	6	7	8
58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	123	4	4	5	6	7	8
59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	123	4	5	5	6	7	8
60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	123	4	5	6	6	7	8
61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	123	4	5	6	7	8	9
62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	123	4	5	6	7	8	9
63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	123	4	5	6	7	8	9
64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	123	4	5	6	7	8	9
65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	123	4	5	6	7	8	9
66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	123	4	5	6	7	9	10
67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	123	4	5	7	8	9	10
68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	123	4	6	7	8	9	10
69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	123	5	6	7	8	9	10
70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	124	5	6	7	8	9	11
71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	124	5	6	7	8	10	11
72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	124	5	6	7	9	10	11
73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	134	5	6	8	9	10	11
74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	134	5	6	8	9	10	12
75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	134	5	7	8	9	10	12
76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	134	5	7	8	9	11	12
77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	134	5	7	8	10	11	12
78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	134	6	7	8	10	11	13
79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	134	6	7	9	10	11	13
80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	134	6	7	9	10	12	13
81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	235	6	8	9	11	12	14
82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	235	6	8	9	11	12	14
83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	235	6	8	9	11	13	14
84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	235	6	8	10	11	13	15
85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	235	7	8	10	12	13	15
86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	235	7	8	10	12	13	15
87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	235	7	9	10	12	14	16
88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	245	7	9	11	12	14	16
89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	245	7	9	11	13	14	16
90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	246	7	9	11	13	15	17
91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	246	8	9	11	13	15	17
92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	246	8	10	12	14	15	17
93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	246	8	10	12	14	16	18
94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	246	8	10	12	14	16	18
95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	246	8	10	12	15	17	19
96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	246	8	11	13	15	17	19
97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	247	9	11	13	15	17	20
98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	247	9	11	13	16	18	20
99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	257	9	11	14	16	18	20

